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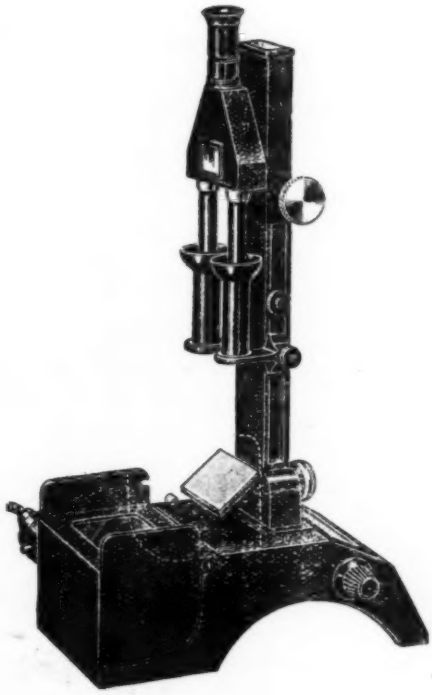

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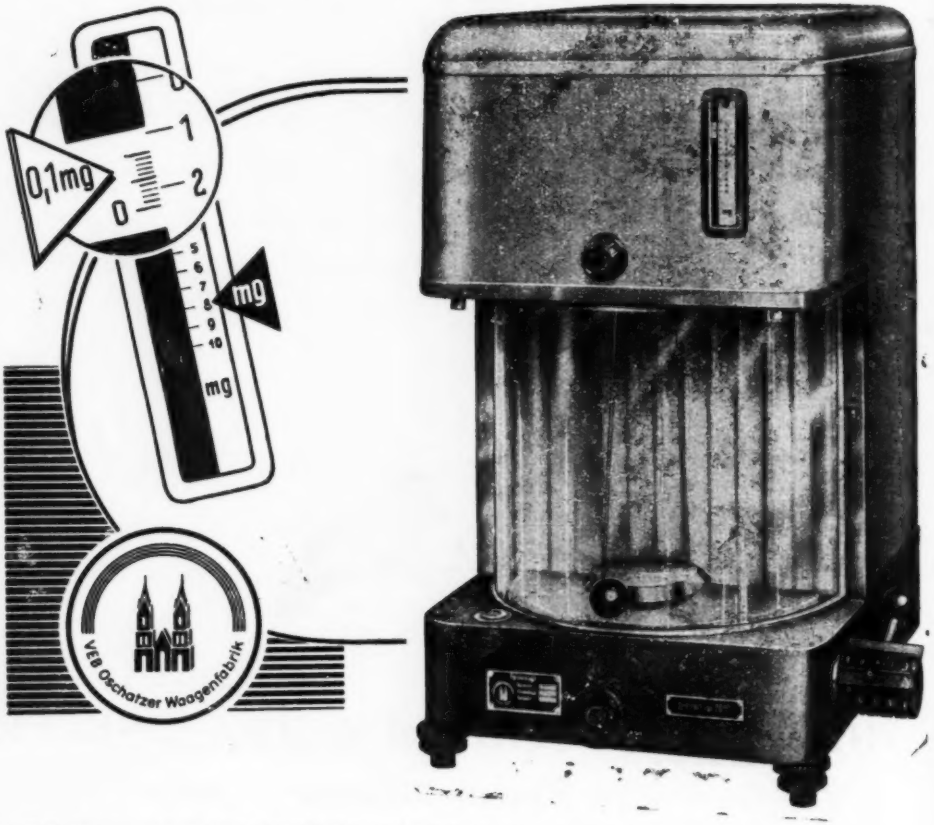

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[Jour. Indian Chem. Soc., Vol. 37, No. 4, 1960]

BENZOYL CHLORIDE AS A POLAR SOLVENT. PART V. CONDUCTOMETRIC TITRATIONS IN BENZOYL CHLORIDE

By Ram Chand Paul, Joginder Singh Johar and Gurdev Singh

Acid base neutralisation reactions between the solvo-acids, like titanium tetrachloride, stannic chloride, zirconium tetrachloride, tellurium tetrachloride and antimony pentachloride, on the one hand, and the solvo-bases, like pyridine, quinoline, α-, β- and γ-picolines and dimethylaniline, on the other, have been carried out in benzoyl chloride, and the course of reactions has been followed conductometrically. The composition of the neutralisation complexes, as isolated and reported earlier (part II), has been confirmed and the existence of quite a few more has been indicated. The conductance of the solutions of solvo-acids and solvo-bases as well as their neutralisation has been explained on the basis of the ionisation of benzoyl chloride as : $BzCl \rightleftharpoons Bz^+ + Cl^-$.

Conductometric titrations have gained considerable importance in the study of acid-base neutralisation reactions in polar solvents (Smith, *Chem. Rev.*, 1938, **23**, 165 ; Gutmann, *Monatsh.*, 1954, **85**, 404 ; *Z. anorg. allgem. Chem.*, 1951, **266**, 331 ; Spandau and Brunneck, *ibid.*, 1955, **278**, 197). Neutralisation reactions between acids and bases, characteristic of the solvo-system benzoyl chloride, have already been described in a previous paper (Paul, Chander and Singh, this *Journal*, 1958, **35**, 869). These reactions have now been studied conductometrically, and the existence of the complexes has been confirmed.

The specific conductances of the solutions of the solvo-bases, such as, α-, β- and γ-picolines and dimethylaniline, and the ansolvo-base, dimethylphenylbenzylammonium chloride, in benzoyl chloride have been determined at 28° The results (Table I) reveal that these solutions are more conducting than the solvent itself (specific conductance = 9×10^{-8} ohm^{-1}-cm^{-1} at 20° ; Gutmann and Tennenberger, *Monatsh.*, 1957, **88**, 216).

TABLE I

Specific conductance of benzoyl chloride = 9×10^{-8} ohm^{-1} cm^{-1} at 20°.

Base.	Concentration (moles/litre).	Sp. conductance (ohm^{-1} cm^{-1}).
α-Picoline	0.0103	2.583×10^{-5}
β-Picoline	0.0100	2.253×10^{-5}
γ-Picoline	0.0100	2.280×10^{-5}
Dimethylaniline	0.0100	4.808×10^{-6}
Dimethylphenylbenzyl-ammonium chloride	0.0016	3.384×10^{-5}

This indicates that on dissolution of these substances in benzoyl chloride, ion pairs are formed which conduct electric current. Therefore, on the basis of the ionisation of benzoyl chloride as:

$$C_6H_5COCl \rightleftharpoons C_6H_5CO^+ + Cl^-$$

and the strongly electron-donor nature of the nitrogen in the tertiary bases, the structure of these solvo-bases in benzoyl chloride solutions can be represented as:

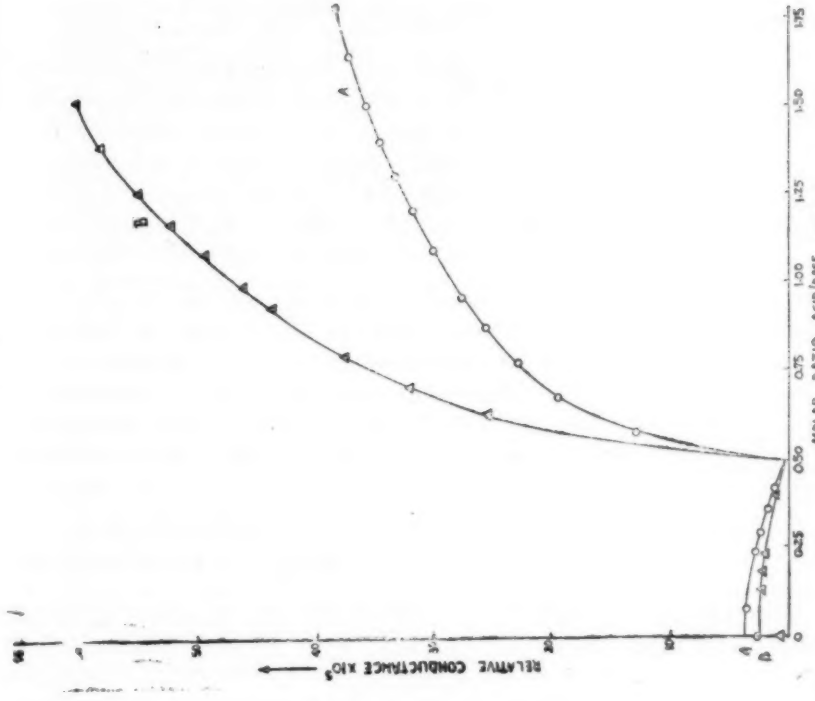
$$B + BzCl \longrightarrow B.BzCl \rightleftharpoons B.Bz^+ + Cl^-$$
$$(Bz = C_6H_5CO).$$

Dimethylphenylbenzylammonium chloride is soluble in benzoyl chloride and in solution it must exist as ions:

$$[(CH_3)_2N.C_6H_5.C_7H_7]Cl \rightleftharpoons (CH_3)_2N^+.C_6H_5.C_7H_7 + Cl^-.$$

Similar observations have been recorded (Gutmann and Tannenberger, *loc.cit.*) in the case of the Lewis acids, such as, stannic chloride, titanium tetrachloride, zirconium tetrachloride and antimony pentachloride. Solutions of these in benzoyl chloride are more conducting than the solvent itself, although some of them, such as, stannic chloride ("International Critical Tables", McGraw Hill Book Co. Inc., N.Y. London, 1926, VI, p. 142) and titanium tetrachloride (Eingorn, *Ukrain Khim. Zhur.*, 1950, **16**, 404), are non-conducting in the pure state. The mode of ionisation of the solutions of these acids and bases in benzoyl chloride has already been proposed (Paul, Chander and Singh, *loc.cit.*). Some conductometric titrations between tetraethylammonium chloride and a few solvo-acids in benzoyl chloride as solvent were carried out by Gutmann and Tannenberger (*Monatsh.*, 1957, **88**, 292). In the present work the neutralisation reactions between the tetrachlorides of tin, titanium, zirconium and tellurium and the pentachloride of antimony as solvo-acids and pyridine, quinoline, α-, β- and γ-picolines and dimethylaniline as solvo-bases have been studied conductometrically. The formation of a number of compounds with different stoichiometric ratios (Paul, Chander and Singh, *loc.cit.*) has been confirmed and the formation of some new compounds has been indicated.

On the addition of a solution of stannic chloride in benzoyl chloride to a solution of α-picoline in the same solvent, a light yellow solid begins to separate, and the conductance of the solution falls progressively till at the point, where the acid/base molar ratio becomes 0.5 (Fig. 1), the conductance is at a minimum and the precipitation is complete. If the addition of the acid solution is continued beyond this point, the precipitate begins to dissolve slowly and the conductance increases rapidly till the second break occurs at the acid/base molar ratio of 1.0. Here the precipitate dissolves completely and the solution becomes clear. On further addition of the acid solution, the rate of increase of the conductance is not appreciable, and no further break in the curve is noticed.



A—Stannic chloride (0.501M/1)/α-picoline (0.0381 g.).
B— " (0.5734M/1)/β- " (0.0479 g.).
C— " (0.3122M/1) γ- " (0.0348 g.).

FIG. 1

A—Stannic chloride (0.6444M/1)/pyridine (0.0327 g.).
B— " (0.7152M/1)/ quinoline. (0.0688 g.).

FIG. 2

During this titration the conductance of the solution records enormous changes. This may be attributed to the addition and removal of ionic species from the reaction medium. The appearance of the precipitate in the beginning of the titration can be ascribed to the formation of *bis*-benzoyl-α-picolinium hexachlorostannate, according to the following reactions:

$$SnCl_4 + 2BzCl \rightleftharpoons 2Bz^+ + SnCl_6^{2-} \text{ (Formation of the solvo-acid)}$$

$$C_6H_7N + BzCl \rightleftharpoons C_6H_7N^+.Bz + Cl^- \text{ (Formation of the solvo-base)}$$

$$2C_6H_7N^+.Bz + 2Cl^- + 2Bz^+ + SnCl_6^{2-} \rightarrow 2BzCl + (C_6H_7N.Bz)_2\,SnCl_6 \text{ (Neutralisation)}$$

The progressive removal of the benzoyl-α-picolinium and the chloride ions from the solution to yield an insoluble precipitate on the addition of stannic chloride solution explains the decrease in the conductance, which reaches a minimum when the precipitation is complete. The rapid rise in conductance as a consequence of the dissolution of the precipitate can be attributed to the formation and subsequent ionisation of the soluble and highly ionised acid salt, benzoyl-α-picolinium benzoylhexachlorostannate,

$$(C_6H_7N.Bz)_2\,SnCl_6 + 2Bz^+ + SnCl_6^{2-} \longrightarrow 2(C_6H_7N.Bz).Bz.SnCl_6$$
$$\rightleftharpoons 2Bz^+ + 2(C_6H_7N.Bz.SnCl_6^-).$$

Thus, the addition of stannic chloride solution increases the number of ions entering the reaction medium, and as a result, the conductance increases considerably. At the second break the dissolution of the precipitate or the conversion of the normal salt to the acid salt is complete, and any further addition to the acid solution has little effect on the conductance, as the solvo-acid, Bz_2SnCl_6, is comparatively feebly ionised.

The conductance curves, obtained by titrating stannic chloride against β-picoline and γ-picoline, are also presented in Fig. 1. In both these cases, two breaks corresponding to acid/base molar ratio of 0.5 and 1.0 are obtained. These breaks may be attributed to the formation of the normal salts, which are insoluble, and the acid salts, which are soluble, in benzoyl chloride. The course of reaction in both these cases can be explained on lines similar to those given for titration with α-picoline.

Pyridine and quinoline have been used as solvo-bases for conductometric titrations in selenyl chloride (Smith, *loc.cit.*), phosphoryl chloride (Gutmann, *Monatsh.*, 1954, **85**, 1077) and thionyl chloride (Spandau and Brunneck, *loc.cit.*). The former forms a monosolvate (Adkins and Thompson, *J. Amer. Chem. Soc.*, 1949, **71**, 2242) while the latter, a disolvate (Paul, Bains and Singh, this *Journal*, 1958, **36**, 489) with benzoyl chloride. The addition of a solution of stannic chloride in benzoyl chloride to a solution of pyridine in benzoyl chloride lowers the conductance of the latter with the immediate separation of a white precipitate (Fig. 2). The continued addition of the stannic chloride solution results in a progressive fall in the conductance which reaches a minimum when the acid/base molar ratio is 0.5. With any further addition of the acid solution, the conductance increases rapidly. At a later stage, however, the rate of increase of conductance falls, but the precipitate does not dissolve completely even when

three times the volume of the acid solution, used at the point of minimum conductance, has been added.

The separation of the precipitate and the decrease in conductance at the beginning of the titration may be considered as due to the formation of the normal salt, *bis*-benzoylpyridinium hexachlorostannate. The reaction can be represented as:

$$C_5H_5N.BzCl \rightleftharpoons C_5H_5N^+.\ Bz + Cl^-$$

$$2(C_5H_5N^+.\ Bz) + 2Cl^- + 2Bz^+ + SnCl_6^{2-} \longrightarrow (C_5H_5N.Bz)_2SnCl_6 + 2BzCl.$$

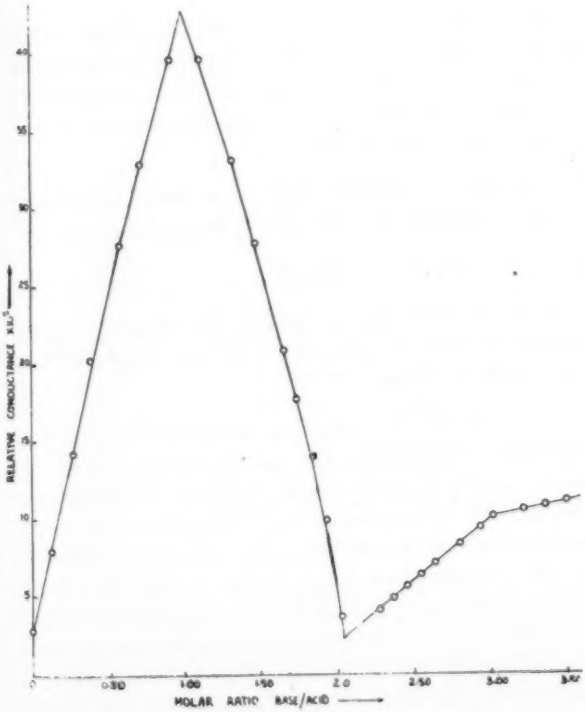
The rise in conductance may be attributed to the formation and ionisation of the acid salt, benzoylpyridinium benzoylhexachlorostannate in solution as:

$$(C_5H_5N.Bz)_2SnCl_6 + 2Bz^+ + SnCl_6^{2-} \longrightarrow 2(C_5H_5N.Bz).Bz.\ SnCl_6$$
$$\rightleftharpoons 2Bz^+ + 2(C_5H_5N.Bz.SnCl_6^-).$$

The difficulty in locating the second break, corresponding to the formation of the acid salt, may be regarded as due to the the sparingly soluble character of the acid salt and the slow formation of the acid salt from the normal salt. The observations recorded in the titration of stannic chloride against quinoline (Fig. 2) are quite similar to those obtained in the titration of pyridine, mentioned above, and can be explained in a similar way. In this case also, only one break corresponding to the formation of the normal salt, *bis*-benzoylquinolinium hexachlorostannate, is observed, although both the normal and the acid salts have been isolated and analysed in partially desolvated forms (Paul, Chander and Singh, *loc.cit.*).

FIG. 3

Dimethylaniline (0.714ö*M*/1) *against stannic chloride* (0.0926 g.).



Dimethylaniline is freely miscible with benzoyl chloride, and therefore has been used as a titrant in its titrations with the solvo-acids. On the addition of the solution of dimethylaniline in benzoyl chloride to that of stannic chloride, a sharp increase in the conductance of thel atter solution is recor ded (Fig. 3). The conductance

reaches its maximum when the base/acid molar ratio is 1.0, and thereafter it begins to decrease rapidly with the simultaneous separation of a white crystalline precipitate. At the base/acid molar ratio of 2.0, the conductance attains its minimum value. If the addition of the base solution is continued further, the conductance again begins to rise. The third break occurs when the base/acid molar ratio is 3.0. Any further addition of dimethylaniline solution increases the conductance only slightly. The explanation for the change in conductance during the titration can be offered on the basis of the existence of ion pairs in solution. The addition of dimethylaniline solution to that of stannic chloride results in the formation of the acid salt, which is soluble in benzoyl chloride and is highly ionised. The conductance of the solution therefore rises rapidly.

$$C_8H_{11}N + BzCl \rightleftharpoons C_8H_{11}N^+.\,Bz + Cl^-$$

$$C_8H_{11}N^+.\,Bz + Cl^- + 2Bz^+ + SnCl_6^{2-} \longrightarrow (C_8H_{11}N.Bz).\,Bz.SnCl_6 + BzCl$$

$$(C_8H_{11}N.Bz).Bz.SnCl_6 \rightleftharpoons Bz^+ + (C_8H_{11}N.Bz.SnCl_6^-)$$

Just after the first break, the formation of the norn al salt begins. This is insoluble and precipitates out. Due to the removal of the ions from the solution, the conductance begins to fall.

$$Bz^+ + (C_8H_{11}N.\,Bz.SnCl_6^-) + C_8H_{11}N^+.\,Bz + Cl^- \longrightarrow (C_8H_{11}N.Bz)_2SnCl_6 + BzCl.$$

At the point of minimum conductance, the precipitation of the normal salt is complete. With further addition of the base, the formation of only slightly dissociated complex with the base/acid molar ratio of 3.0 starts and the conductance begins to increase. This is complete at the third break and thereafter the slow increase in conductance is due to addition of dimethylaniline solution only.

Titanium tetrachloride is soluble in benzoyl chloride only to a small extent and affords a monosolvate (Cullinane *et al.*, *J. Chem. Soc.*, 1952, 4106), which ionises as:

$$TiCl_4.BzCl + BzCl \rightleftharpoons 2Bz^+ + TiCl_6^{2-}.$$

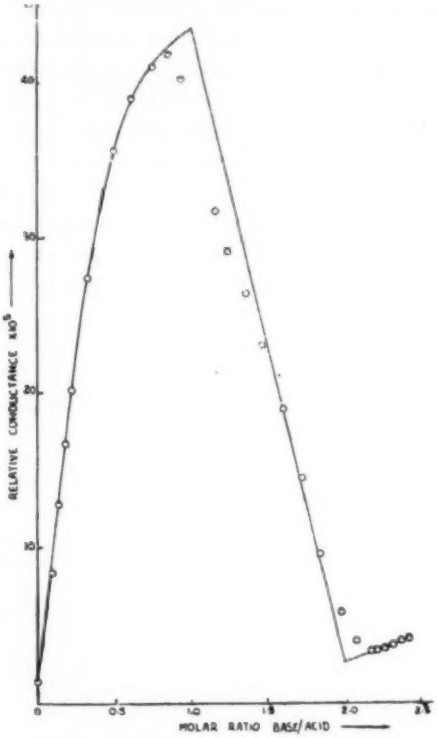
α-Picoline, on the other hand, is appreciably soluble in benzoyl chloride and solutions of fairly high concentration can be prepared. In the titration that follows, therefore, α-picoline has been used as a titrant.

On the addition of a solution of α-picoline in benzoyl chloride to that of titanium tetrachloride, the conductance increases progressively (Fig. 4). It reaches a maximum as the base/acid molar ratio becomes 1.0 and then begins to fall rapidly as a consequence of the separation of a yellow precipitate. The precipitation is complete at the base/acid molar ratio of 2.0 and the conductance is at its minimum. If the addition of α-picoline solution is continued, the conductance again begins to rise. The curve shows two breaks corresponding to the formation of the acid salt, benzoyl-α-picolinium benzoylhexachlorotitanate, and the normal salt, *bis*-benzoyl-α-picolinium heaxchlorotitanate. The former, being highly ionised, is responsible for the rapid increase in the conductance in the beginning of the titration. However, due to the limited

solubility of the salt, it begins to go out of the solution phase as a yellow precipitate near the first break. Some points recorded near the first break therefore do not fall

FIG. 4

α-Picoline (0.3684 *M*/1) *against* $TiCl_4$ (0.1062 g.).



on the regular curve. The rapid decrease in the conductance after the first break is due to the removal of the ions from the solution on account of the formation of the insoluble normal salt. After the second break, the slow rise in conductance is due to the addition of the weakly ionised benzoyl-α-picolinium chloride solution. The formation of the acid salt and its subsequent ionisation may be represented as:

$$2Bz^+ + TiCl_6^{2-} + C_6H_7N^+.Bz + Cl^- \rightarrow (C_6H_7N.Bz).Bz.TiCl_6 + BzCl$$
$$(C_6H_7N.Bz).Bz.TiCl_6 \rightleftharpoons Bz^+ + (C_6H_7N.Bz.TiCl_6^-).$$

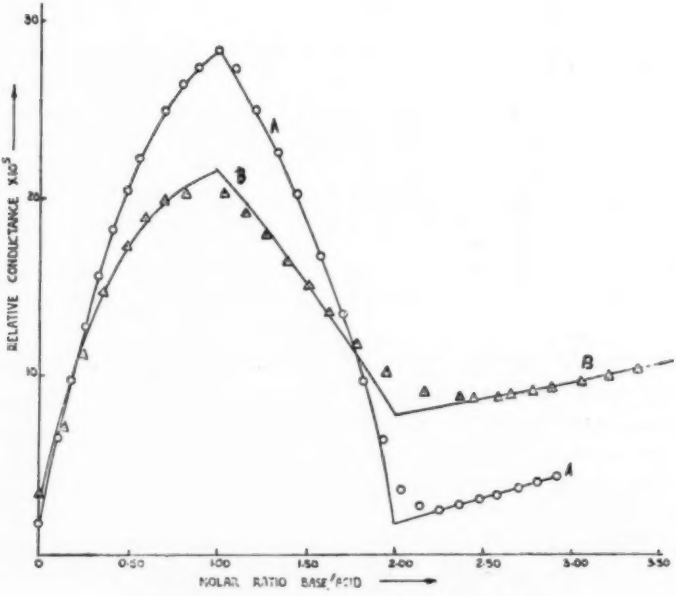
The formation of the normal salt can be represented as:

$$Bz^+ + (C_6H_7N.Bz.TiCl_6^-) + C_6H_7N.^+Bz + Cl^- \rightarrow (C_6H_7N.Bz)_2TiCl_6 + BzCl.$$

The tetrachlorides of tellurium and zirconium, like those of tin and titanium, behave as dibasic acids in benzoyl chloride. These do not form any solid solvates under ordinary

experimental conditions with benzoyl chloride (Paul, Bains and Singh, *loc.cit.*), but the existence of their solvates in solution is indicated by the high conductance of their solution. On account of the limited solubility of these tetrachlorides, the bases have been used as titrants.

The curves obtained for the titrations of α-picoline against tellurium tetrachloride (Fig. 5) and zirconium tetrachloride (Fig. 6) are quite similar to that obtained in the case of the titration of α-picoline against titanium tetrachloride. The curve in each case shows two breaks corresponding to the formation of the acid salt at the base/acid molar ratio of 1.0 and the normal salt at the base/acid molar ratio of 2.0. The acid salts, benzoyl-α-picolinium benzoylhexachlorotellurite and benzoyl-α-picolinium benzoylhexachlorozirconate, are soluble and ionised, while the normal salts, *bis*-benzoyl-α-picolinium hexachlorotellurite and *bis*-benzoyl-α-picolinium hexachlorozirconate, are insoluble and separate out as white solids. The explanation advanced in the case of the neutralisation of α-picoline with titanium tetrachloride is applicable in these cases also.

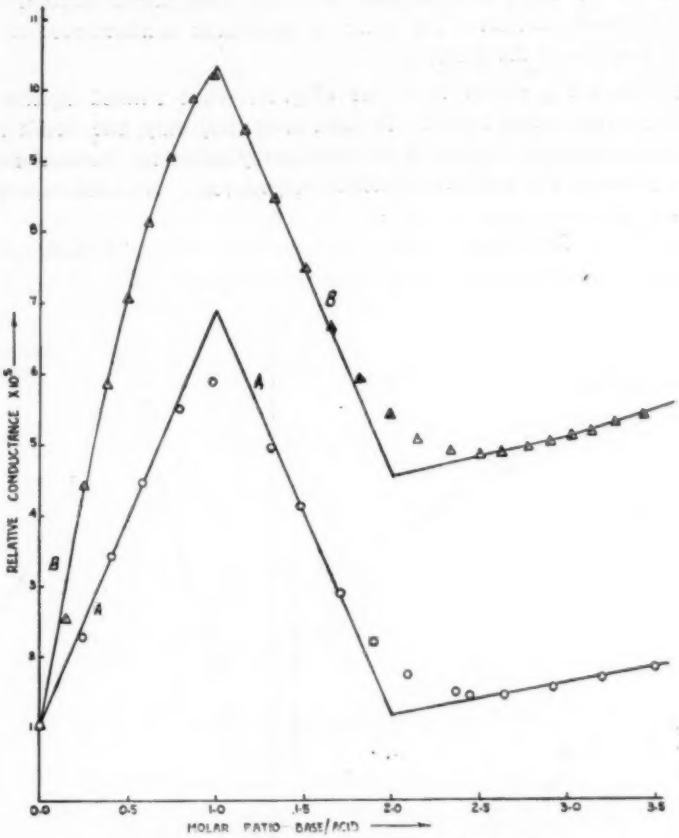


A—α-Picoline (0.2875 *M*/l)/$TeCl_4$ (0.0671 g.).
B—Dimethylaniline (0.4203 *M*/l) ,, (0.0663 g.).

The observations recorded in the titrations of dimethylaniline against tellurium tetrachloride (Fig. 5) and zirconium tetrachloride (Fig. 6) are similar to those obtained in the titration of this base against stannic chloride. In both the cases three breaks corresponding to the base/acid molar ratios of 1.0, 2.0 and 3.0 are noticed in the conduc-

tance curves. The course of reaction is similar to that of the neutralisation of stannic chloride against dimethylaniline, and can be explained on similar grounds.

FIG. 6



A. α-Picoline (0.1967*M*/l)/$ZrCl_4$ (0.0108 g.).
B. Dimethylaniline (0.2277*M*/l)/$ZrCl_4$ (0.0308 g.).

Antimony pentachloride acts as a strong monobasic acid in benzoyl chloride and furnishes a monosolvate (Seel, *Z. anorg. Chem.*, 1943, **252**, 24; Paul Bains and Singh, *loc.cit.*) with this solvent, which is dissociated and is soluble in excess of benzoyl chloride. Its dissociation may be represented as :

$$SbCl_5.BzCl \rightleftharpoons Bz^+ + SbCl_6^-.$$

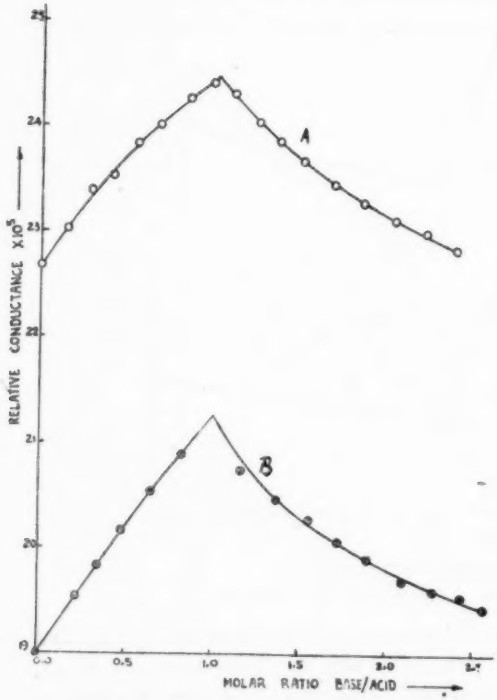
The initial conductance of the acid solution arises from the dissociation of this solvate, but when a solution of quinoline in benzoyl chloride is added dropwise (Fig. 7), the conductance of the solution increases, which means that a more ionogenic compound is formed.

$$Bz^+ + SbCl_6^- + C_9H_7N^+.Bz + Cl^- \rightarrow (C_9H_7N.Bz)SbCl_6 + BzCl$$
$$(C_9H_7N.Bz)SbCl_6 \rightleftharpoons (C_9H_7N^+.Bz) + SbCl_6^-$$

As the addition of quinoline solution is continued, the conductance rises progressively until it reaches a limiting value corresponding to the formation of a 1:1 complex, benozoylquinolinium hexachloroantimonate, and then falls off beyond this point. No further break in the curve is observed. The yellowish brown solution of antimony pentachloride becomes colorless at the point of maximum conductance and no precipitate appears throughout the titration.

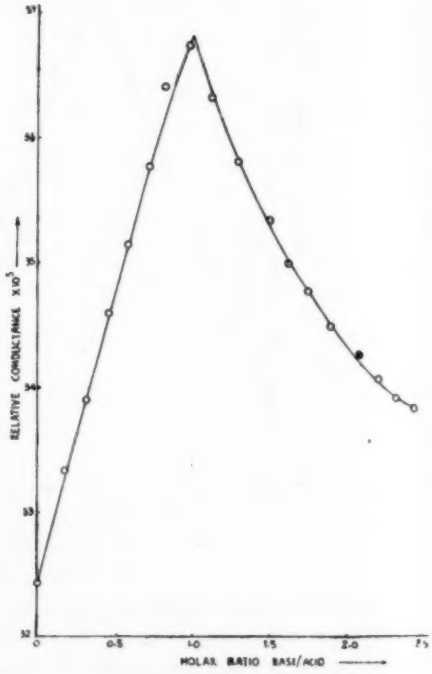
Dimethylaniline (Fig. 7) and α-picoline (Fig. 8), when titrated against antimony pentachloride, provide similar curves. In these cases also, only one break is observed and can be ascribed to the formation of benzoyldimethylanilinium hexachloroantimonate and benzoyl-α-picolinium hexachloroantimonate respectively. No solid separates during the titration.

FIG. 7



A. Dimethylaniline (0.2571*M*/l)/$SbCl_5$ (0.0411 g.).
B. Quinoline (0.2384 „)/ „ (0.0383 g.).

FIG. 8



α-Picoline (0.3176*M*/l) against $SbCl_5$ (0.0681 g.).

EXPERIMENTAL

Benzoyl chloride and the acids and bases were purified as already described (Paul, Bains and Singh, *loc cit.*; Paul, Chander and Singh, *loc. cit.*). For the present work benzoyl chloride, purified as above, was again distilled in a special fractionating column and collected at a take-off ratio of 1:5.

For measurements of the specific conductance of the solutions of different bases in benzoyl chloride, special conductivity cell with a cell constant of 0.64, kept at a constant temperature of 28°, was used.

The solutions were prepared in a dry box and the transfer of the solutions was carried out with the help of dry nitrogen under pressure. For conductometric titrations a glass conductivity cell, equipped with a microburette, replaceable platinum electrodes and calcium chloride guard tube, was employed. The resistance of the solutions was measured at 28° by using a precision measuring bridge type WBR No. 108 with logarithmic indicator amplifier type, TAV. IKC, No. 034 (Wissenschaftlich-Technische Werkstatten, Wielheim/Oby., Germany).

In Figs. 1-8, molar ratio of acid to base or base to acid has been plotted against relative conductance which is equal to $1/R$. Cell constant has not been taken into account due to the difficulty of placing the electrodes in exactly the same positions in the cell.

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ACIDOID BEHAVIOUR OF CHARCOAL AS A FUNCTION OF ITS OXYGEN COMPLEXES. PART IV. MOISTURE ADSORPTION, HEAT OF WETTING AND EVACUATION OF CHARCOAL WITH DIFFERENT METAL CATIONS

By Balwant Rai Puri, Krishan Murari and D. D. Singh

The replacement of surface H^+ ions by different alkali and alkaline earth cations, such as Li^+, Na^+, Mg^{2+}, Ca^{2+} and Ba^{2+}, results in making the charcoal surface more hydrophilic, as indicated by water-vapour adsorption isotherms and heats of immersion in water. The effect is more for monovalent than for bivalent cations and increases with increase in the amount of the cation introduced. The results of analysis of the gases, evolved on evacuating the charcoals with different amounts of the various cations, support the view that the acid character of charcoal is due to the presence of CO_2-complex, on account of which it undergoes surface ionisation in water, yielding H^+ ions directed towards the liquid phase.

It has been shown in previous communications (Puri *et al.*, this *Journal*, 1957, **34**, 357; 1958, **35**, 189) that charcoal on account of the existence of CO_2-complex along its surface undergoes surface ionisation in water as:

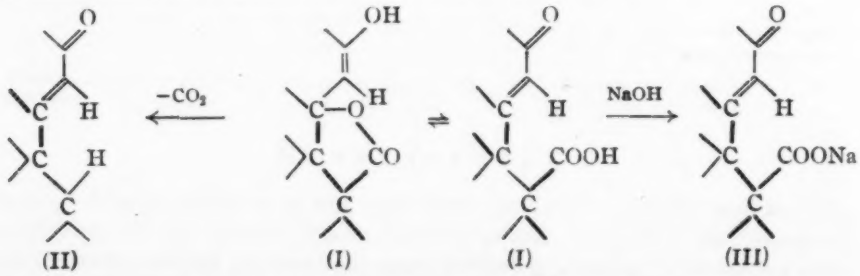
$$\text{O-}CO_2 + H_2O \longrightarrow \text{O-}CO_3^{2-} \vdots\, 2H^+ \qquad \ldots \qquad (1)$$

where the circle represents the charcoal surface and -C a surface carbon atom. The surface hydrogen ions, being directed towards the liquid phase, can bring about neutralisation of alkalies in accordance with the equation:

$$\text{O-}CO_3^{2-} \vdots\, 2H^+ + 2MOH \longrightarrow \text{O-}CO_3^{2-} \vdots\, 2M^+ + 2H_2O \qquad \ldots \qquad (2)$$

The metal cations have been actually located on the charcoal surface even after washing and drying, and it has been shown that these can be exchanged for other cations by suitable treatments (Puri *et al.*, *J. Sci. Ind. Res.*, 1958, **17B**, 188). It was thought of interest to study the effect of different metal cations on such surface characteristics of charcoal as moisture-adsorption capacity and heat of immersion in water.

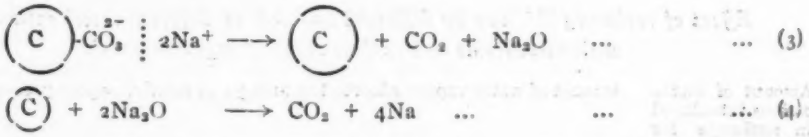
There is another aspect of the problem. Garten and Weiss (*Austral. J. Chem.*, 1957, **10**, 295) in order to explain the base adsorption by charcoal and the evolution of an equivalent amount of CO_2 from it on evacuation, first reported by Puri *et al.* (*Chem. & Ind.*, 1956, B.I.F.R., 30), suggested the presence of lactone groups at the charcoal surface, and represented the reactions involved as:



(II) (I) (I) (III)

the keto group accounting for the liberation of carbon monoxide.

Now, according to this mechanism, the corresponding salt of the acid (III in the above equation) on degassing at high temperatures should evolve the same amount of carbon dioxide as the original charcoal, while, if it is formed according to the mechanism represented by equation 2, it should evolve more carbon dioxide than the original charcoal, as shown below :



$$\text{(C)}\text{-}CO_3^{2-} \vdots 2Na^+ \longrightarrow \text{(C)} + CO_2 + Na_2O \quad \ldots \quad \ldots \quad (3)$$

$$\text{(C)} + 2Na_2O \longrightarrow CO_2 + 4Na \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

the metallic oxide reacting at the prevailing high temperature with carbon to produce an equivalent amount of carbon dioxide in addition.

This point can be verified by evacuating charcoal before and after replacing surface H^+ ions with different amounts of different metal cations.

The work described in this paper was undertaken with these objectives in view.

Experimental

Sugar charcoal, prepared by carbonisation of recrystallised cane sugar with H_2SO_4 (conc.), followed by exhaustive washings with water, was used. Its base-adsorption capacity (b.a.c.), as determined by shaking 1 g. with 100 c.c. of 0.2*N*-$Ba(OH)_2$ solution for about 24 hours in the usual way, was found to be 674.8 m.e. per 100 g. The H-charcoal was then converted into Li^+-, Na^+-, Ba^{2+}-, Ca^{2+}- and Mg^{2+}- charcoals by shaking 10 g. portions with increasing amounts of 0.2*N* solutions of the corresponding alkalies (using solid CaO and MgO for preparing Ca- and Mg-charcoals). The amounts of alkalies added were well within the base-neutralising capacity of the charcoal. The suspensions were refluxed for about 8 to 10 hours, followed by shaking for 48 hours. The clear supernatant liquid was decanted off and the charcoal was washed repeatedly with CO_2-free distilled water to remove unchanged alkali, if any. The amounts of the various cations introduced into the charcoal complex were determined by shaking 1 g. samples (oven-dried at 110°) with 100 c.c. of 0.1*N*-HCl for about 24 hours and estimating the amount of lithium chloride and sodium chloride brought into solution by evaporating an aliquot of the clear supernatant liquid to dryness, and those of magnesium, calcium and barium by the usual gravimetric procedures.

A sample of charcoal was also activated in steam at 1000° under optimum conditions (Singh *et al.*, *Indian J. Appl. Chem.*, 1958, **21**, 187).

Water Isotherms and Surface Area.—Water vapour adsorption isotherms were determined at 25° by the procedure described before (Puri *et al.*, this *Journal*, 1952, **29**, 841). Surface areas were calculated from the isotherms by the method suggested by Harvey (*J. Amer. Chem. Soc.*, 1943, **65**, 2343).

Heats of Immersion.—Charcoal samples (2-4 g.) were taken into thin-walled glass bulbs and outgassed for about 2 hours at the room temperature. The heat of immersion was determined by breaking these bulbs in excess (300 c.c.) of water by following the technique described by Boyd and Harkins (*ibid.*, 1942, **64**, 1190).

Evacuation at 1200°.—The various samples of charcoal (2 g. portions) were subjected to evacuation at 1200° in a resistance-tube furnace and the gases evolved were analysed in an Orsat-Lunge gas-analysis apparatus in the usual manner.

TABLE I

Effect of replacing H^+ *ions by different amounts of different metal cations on water isotherms and surface areas of sugar charcoal.*

Amount of metal cations introduced in exchange for H^+ ion (m.e./100 g.).	Amount of water vapour adsorbed (g./100 g.) at relative vapour pressure.						Surface area ($m.^2/g.$)
	0.10.	0.30.	0.50.	0.70.	0.90.	0.99.	
0.00 (H-charcoal)	2.61	5.26	9.73	12.21	18.70	27.55	421.0
Li^+-charcoal							
121.0	5.58	7.12	10.58	13.01	26.34	40.50	401.2
157 3	7.24	9.44	12.86	18.79	29.48	47.32	426.5
229.9	8.62	12.50	16 74	22 58	37.81	66.64	400.1
266.2	9.91	12.68	18.81	24.02	40.12	72.66	440.2
438.8	11.03	14.31	20.01	26.09	45.90	80.56	430.8
Na-charcoal							
96.8	5.20	7.21	10.19	13.53	25.76	40.20	400.4
114.4	7.12	9.49	11.26	17.50	28.04	61.00	398.4
198.1	8.32	9.81	12.04	17.84	29.79	65.33	409.1
220.0	9.01	10.25	16.74	21.70	35.72	70.18	416.5
448.9	10.98	12.39	17.01	22.68	36.94	76.89	406.8
Mg-charcoal							
135.8	4.41	7.25	10.62	11.78	19.95	28 11	416.8
232.5	6.36	9.01	11.42	12.59	21.90	32.04	44[illegible].2
409.0	9.30	11.42	14.10	17.56	27.62	37.82	399.2
Ca-charcoal							
145.2	4.01	6.75	10.14	14.16	20.32	29.20	399 7
169.4	5.10	7.56	11.41	14.59	21.10	30.24	405.6
411.4	7.51	9.42	12.21	15.82	25.24	36.24	433.9
Ba-charcoal							
133.0	4.00	5.61	9.79	12.51	18.76	29.50	426.2
217.8	4.71	7.02	10.82	13.62	20.06	30.15	410 8
425.6	7.10	9.82	13.22	16.23	23.56	33.58	430.8
Steam-activated charcoal	3.72	13.95	15.72	28.91	36.36	45.27	...

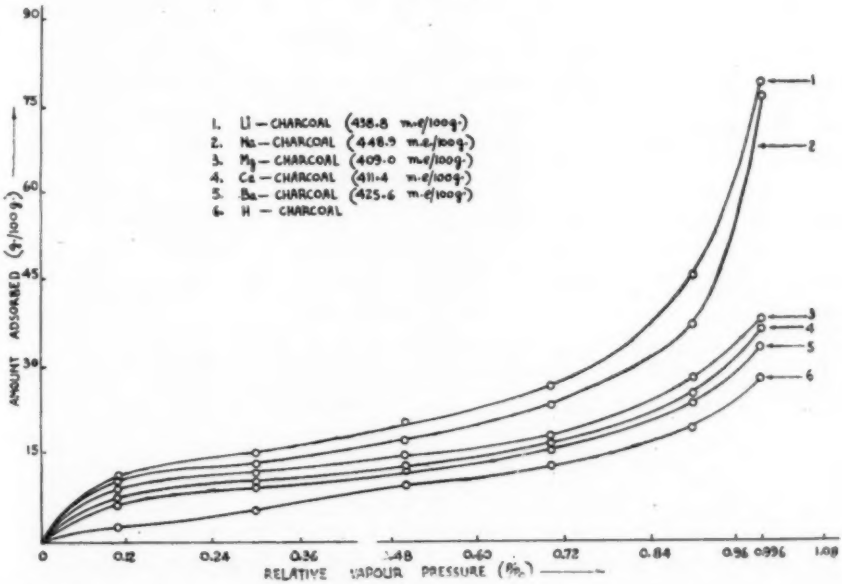
DISCUSSION

From Table I it appears that the moisture-adsorption values increase at all relative vapour pressures on the replacement of H^+ ions by increasing amounts of different metal cations, and that the effect is more in case of monovalent than in the case

of bivalent cations. The replacement of H^+ ions to the extent of about 440 m.e./100 g. (out of total base-exchange capacity of 675 m.e./100 g. of the charcoal) for instance, causes two-fold to three-fold increase in the moisture-adsorption capacity of the charcoal from the atmospheres of different relative humidities. It is also interesting to note that the adsorption values, obtained on the introduction of Li^+ or Na^+, are even higher than those obtained on activating the charcoal in steam at 1000° under optimum conditions. This shows that the introduction of alkali cations makes the charcoal surface extremely hydrophilic. At the same time this places at our disposal a very convenient method for preparing an efficient water-adsorbent charcoal.

Since the surface area of charcoal undergoes little or no change on the replacement of H^+ ions by different metal cations (Table I, last column), the increase in moisture-adsorption capacity of charcoal cannot be attributed to this factor. The increase is probably due to the greater surface ionisation of charcoal with metal cations than that of H-charcoal on analogy with greater dissociation of alkali salts of weak acids than that of the acids themselves.

FIG. 1



The comparative effect of the various metal cations is brought out clearly in Fig. 1, in which the isotherms of charcoal containing nearly the same amounts of different cations have been plotted. It is evident that lithium produces maximum increase, followed closely by sodium. Magnesium-, calcium- and barium-charcoals afford lower values probably due to smaller ionisation on analogy with the salts of these bases. The difference may also be partly due to a smaller degree of hydration of these ions. It is interesting to note in this connection that the effect of the various cations decreases in about the same order as their degree of hydration.

The replacement of H^+ ions by other cations also causes an appreciable increase in the heat of immersion of charcoal in water (Table II), the increase, for a given cation, being in proportion to its amount, as is evident from the values recorded in the last column of Table II. The effect per m.e. is maximum in the case of lithium, followed closely by sodium, and is minimum in the case of maguesinm and barium, which provide almost identical values. These results are in accord with those obtained for the moisture adsorption, recorded in Table I.

TABLE II

Heat of immersion of different samples of charcoal in water.

Amount of metal cations introduced in exchange for H^+ ions.	Heat of immersion.	Increase in heat per m.e. of the cation introduced.	Amount of metal cations introduced in exchange for H^+ ions.	Heat of immersion.	Increase in heat per m.e. of the cation introduced.
0.00 (H-charcoal)	1625.3	...	...	...	...
Li-charcoal.			**Mg-charcoal.**		
121.0 m.e./100 g.	2628.7 cal./100 g.	8.26 cal.	135.8 m.e./100 g.	2162.1 cal./100 g.	3.96 Cal.
157.3	2965.5	8.52	232.5	2532.3	3.90
229.9	3579.4	8.50	409.0	3255.5	3.98
266.2	3884.6	8.45	**Ca-charcoal**		
438.8	5289.2	8.35	145.2	2402.4	5.35
			169.4	2557.3	5.50
			411.4	3847.4	5.41
Na-charcoal.			**Ba-charcoal.**		
96.8	2306.7	7.05			
114.4	2437.5	7.10	133.0	2130.3	3.80
198.1	3029.9	7.09	217.8	2480.5	3.92
220.0	3196.1	7.14	425.6	3327.3	4.00
448.9	4816.9	7.11			

In order to see if the replacement of surface H^+ ions by the metal cations has produced any permanent change in the surface characteristics, all the samples of sodium charcoal were converted back into H-charcoal by leaching with dilute hydrochloric acid, followed by repeated washings with water. The moisture-adsorption capacity and the heat of wetting in every case were found to be the same as those of the original charcoal. These H-charcoals were then reconverted into sodium charcoals and the values were again found to increase to their previous levels. It is evident therefore that the charcoal surface does not undergo any permanent change; its characteristics at any time depend upon the nature and the amount of the surface cations held by it.

TABLE III

Gases evolved on evacuating different samples of charcoal containing different amounts of different cations at 1200°.

Amount of metal cations introduced in exchange of H^+ ions (m.e./100 g.).	Gases evolved (in mg./g.) on evacuation at 1200°.				Increase in CO_2 evolved (mg./g.).	Increase in CO_2 expected theoretically (mg./g.).
	CO_2.	CO.	H_2O.	H_2.		
0.0 (H-charcoal)	148.46	120.63	125.50	13.51	...	...
Li-charcoal						
121.0	177.88	119.89	126.65	13.50	29.42	26.62
157.3	182.27	120.49	124.98	13.51	33.81	34.61
229.9	201.08	121.05	125.50	12.05	52.62	50.58
265.2	208.51	120.80	125.50	12.90	60.05	58.56
438.8	244.15	120.50	124.80	13.15	95.70	96.54
Na-charcoal						
96.8	171.31	121.05	126.58	13.51	22.85	21.30
114.4	173.36	121.00	126.00	13.49	24.90	25.17
198.1	194.01	120.63	125.90	13.40	45.55	43.58
220.0	198.47	120.10	125.55	13.55	50.01	48.40
448.0	248.40	121.68	126.90	13.50	99.94	98.76
Mg-charcoal						
135.8	177.51	119.89	124.95	12.60	29.05	29.88
232.5	202.39	120.63	126.80	13.69	53.93	51.15
409.0	238.61	120.60	125.50	12.85	90.15	89.98
Ca-charcoal						
145.2	180.95	121.60	125.95	13.50	32.49	31.94
169.4	185.43	121.05	124.99	13.55	36.07	37.27
411.4	241.36	121.15	125.50	13.69	92.90	90.51
Ba-charcoal						
133.0	178.61	120.69	126.01	13.51	30.15	29.26
217.8	198.46	121.00	125.59	13.99	50.00	47.92
425.6	243.27	120.89	125.91	13.55	94.81	93.63

The results of analysis of the gases, evolved from the various samples of charcoal on evacuation at 1200°, are recorded in Table III. It is seen that there is little or no change in the amounts of CO, H_2O and H_2 evolved on the introduction of different cations However, an appreciable increase in the amount of CO_2 is noticed. This indicates that the mechanism of base adsorption, as postulated by Garten and Weiss (*loc. cit.*), may not be quite correct. It appears more likely that the mechanism proposed by Puri *et al.* (*loc. cit.*), as represented by equation (2), is nearer the truth. This view receives further support from the fact that the increase in the value of CO_2 evolved, as calculated from the amounts of the cations held by the charcoal, in

accordance with equation (4), is quite close to the increase actually observed in every case with the exception of magnesium charcoal, where the increase actually observed is less than that expected theoretically. This discrepancy is understandable since it is well known that magnesium oxide does not part with its oxygen readily even at high temperatures.

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A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF THIOCARBAMIDE

By Prakash Chandra Gupta

A new method for the volumetric determination of thiocarbamide with iodine and bicarbonate buffer is described.

Several methods have been proposed from time to time for the determination of thiocarbamide, mostly based on its desulphurisation or complex formation with metal ions or its oxidation with various oxidising agents. None of them has been found to be entirely satisfactory. Most of the methods require extremely dilute solutions of thiocarbamide to be titrated and are very sensitive to slight variation of experimental conditions or are time-consuming. The external end-point used in Volhard's method is not sufficiently sharp to provide accurate results. Oxidation with permanganate does not afford a satisfactory means of determining thiocarbamide (Cuthill and Atkins, *J. Soc. Chem. Ind.*, 1937, **65**, 5T). Cuthill *et al.* also observed that in oxidation with chloramine-T in neutral solution, the oxygen consumption was less than the theoretical quantity. Moreover, oxidation with chloramine-T proved to be too sensitive to slight variations in experimental conditions to be useful. Oxidation with alkaline hypoiodite is also not very satisfactory, and oxidation with ceric sulphate or potassium dichromate in acid solution requires boiling under reflux and has other unsatisfactory features (Cuthill and Atkins, *loc. cit.*). That Mahr's method (*Z. anal. Chem.*, 1939, **117**, 91), employing bromide-bromate mixture does not yield accurate or reproducible results has been shown by Appa Rao and Neelakantam (*Indian J. Pharm.*, 1952, **14**, 50). The iodimetric method of Werner (*J. Chem. Soc.*, 1912, **101**, 2166) though simplest in technique and therefore most extensively used for thiocarbamide estimations, suffers from the disadvantage that the end points are not always sharp and the results are accurate only when the amount of thiocarbamide present does not exceed 0.2 g./litre. Later modifications of the iodimetric method by Cuthill and Atkins (*loc. cit.*) also did not prove very useful. In view of these facts, the determination of thiocarbamide was reinvestigated.

The oxidation of thiocarbamide by iodine was tried under diverse experimental conditions in various media. It has now been found that thiocarbamide can be estimated more accurately in dilute or strong solutions by using iodine in presence of a bicarbonate buffer. The end-point of the reaction was observed by all the following three techniques, which further adopted the present reaction to a variety of conditions in which thiocarbamide might have to be estimated :

(*a*) Visually—disappearance of iodine colour itself or the blue colour with starch solution.

(*b*) Potentiometrically— when a sudden fall in the E. M. F. of the system occurs near the equivalence point.

(*c*) By employing excess of oxidant and back-titrating the excess of iodine with standard arsenious oxide solution.

The corresponding amounts of thiocarbamide and iodine showed that the thiocarbamide was completely oxidised to urea and sulphate. The reaction involved may be represented as:

$$CS(NH_2)_2 + 4\,I_2 + H_2O \xrightarrow{NaHCO_3} CO(NH_2)_2 + Na_2SO_4.$$

The effect of the quantity of bicarbonate as well as the concentration of thiocarbamide over a wide range has been investigated. Experiments were also conducted taking an excess of iodine solution, adding to it a known volume of thiocarbamide solution and titrating back the excess oxidant with arsenious oxide solution. The use of arsenious oxide in these estimations is of great advantage as it is obtainable in a very pure form and its solutions are stable even on long standing (*Analyst*, 1950, **75**, 577); besides it serves as a direct primary standard for a rapid and accurate determination of iodine. This eliminates the need of prior standardisation of iodine solution. As will be seen from the results (Tables I to VI) thiocarbamide can be accurately estimated by all these techniques.

Experimental

Titrations using Starch End-points (*Visual observation of end-point*).—In each case, iodine solution (20 c.c.) of known strength was taken in a 250 c.c. conical flask and a 10% solution of 'Analar' $NaHCO_3$ (20 c.c.) added. Thiocarbamide solution was then added dropwise from the burette and the end-point observed visually as usual by adding starch solution near the end-point. Results are presented in Table I.

Table I

(End-point observed visually)

$CS(NH_2)_2$ soln. taken.	Iodine soln. (20 c.c. taken).	Eq. vol. of thiocarbamide soln.	$CS(NH_2)_2$ found	
0.1170 g./litre	0.01392 *N*	22.85 c.c.	0.1159 g./litre	99.08%
0.4680	0.05500	22.40	0.4673	99.84
0.7600	0.08913	22.40	0.7572	99.63
1.1624	0.09391	15.40	1.1605	99.83
1.2120	,,	14.80	1.2075	99.63
1.9980	,,	8.95	1.9970	99.94
,,	0.1040	9.90	1.9992	100.08

Potentiometric Titration.—A Ni-Fe cell, capable of producing a constant potential of 4 or 6 volts, was employed as a convenient and reliable source of current for the potentiometer for preliminary adjustments, and a moving coil mirror-galvanometer with lamp and scale, for finer adjustments, were included in the circuit through a double pole double-throw switch. The 'unknown cell' was made of three parts: (*i*) a platinum wire which served as an indicator electrode, (*ii*) a saturated calomel electrode, serving as the reference electrode, and (*iii*) the salt bridge, obtained by filling a jelly of 3% agar in a saturated potassium chloride solution. Cambridge (Pye) Instrument in which

the E.M.F. was read directly on the dial was employed as the potentiometric system. The instrument was always standardised prior to actual experiments, with the help of a Weston cadmium cell. The end-point or the equivalence point was detected quite easily by a sudden and large change in potential which occurred very close to the equivalence point or by calculating $\Delta E/\Delta V$, *i.e.*, the change in E.M.F. per unit volume, as proposed by Hostetter and Roberts (*J. Amer. Chem. Soc.*, 1919, **41**, 1337), $\Delta E/\Delta V$ being maximum near the equivalence point.

The potentiometric titrations of thiocarbamide against standard iodine solutions were performed in the following manner. To an aliquot of iodine solution, taken in a 150 c.c. Pyrex beaker, a known volume of the buffer (viz., a 10% solution of sodium bicarbonate) was added. The titration vessel was kept in cold water to avoid any loss of iodine. The platinum electrode was dipped into the solution. The 'unknown cell' was placed in position A or B and the initial E.M.F. was measured by adjusting the slide-wire contact to zero deflection in the galvanometer. The thiocarbamide solution was run in slowly dropwise and after each addition the solution was stirred well and the potential value noted. Near the equivalence point, the titration was performed with dropwise addition of the thiocarbamide solution with vigorous stirring. In the beginning a gradual decrease in the potential was observed which showed a sudden fall at the equivalence point. After this the E.M.F. changed very slowly when an excess of the thiocarbamide solution was added. Observations of a typical experiment (marked with an asterisk in Table III) are represented in Table II. Influence of (*i*) sodium bicarbonate buffer added, (*ii*) thiocarbamide concentration and (*iii*) iodine concentration was investigated. The results of various experiments have been summarised in Tables III, IV and V.

TABLE II

[0.09391 *N*-Iodine soln. (20 c.c.) + 10% $NaHCO_3$ (20 c.c.)]

Thiocarbamide added.	*E/MVS.*	$\Delta E/\Delta V$.	Thiocarbamide added.	*E/MVS.*	$\Delta E/\Delta V$.	Thiocarbamide added.	*E/MVS.*	$\Delta E/\Delta V$.
					4.70			60.00
0.00 c.c.	368.5		5.00 c.c.	351.3		8.80 c.c.	301.0	
		3.00			6.00			153.00
0.50	367.0		6.00	345.3		8.90	285.7	
		3.00			7.10			*1183.00*
1.00	365.5		7.00	338.2		9.00*	167.4	
		3.30			11.60			35.80
2.00	362.2		8.00	326.6		9.50	149.5	
		2.90			24.00			20.00
3.00	359.3		8.50	314.6		10.00	139.5	
		3.30			38.00			10.50
4.00	356.0		8.70	307.0		11.00	129.0	

* Vol. of thiocarbamide soln. equivalent to the iodine soln. taken.
Observed = 9.00 c.c. Calc. = 8.9449 c.c.

TABLE III

Effect of sodium bicarbonate added.

Thiocarbamide soln. added = 1.998 g./litre. 0.9391 *N*-Iodine soln. taken = 20 c.c.

10% $NaHCO_3$ added (c.c.)	0.0	5.0	10.0	*20.0	30.0	40.0	50.0	60.0	70.0
$CS(NH_2)_2$ found (g/litre)	...	1.8424	1.9856	1.9856	1.0856	1.9856	1.9856	1.9856	1.9856
" %	...	92.2	99.4	99.4	99.4	99.4	99.4	99.4	99.4

* Full details of this experiments are presented in Table II

It has been observed that whereas too small an amount of the bicarbonate causes incomplete oxidation of thiocarbamide, too large an excess of it has little adverse effect on the accuracy of the results. Presence of small amounts of sodium carbonate interferes.

TABLE IV

Effect of thiocarbamide concentration.

Amount of thiocarbamide Taken (g./litre).	Found.		Amount of thiocarbamide Taken (g./litre)	Found.	
0.1170	0.1159 g./litre	99.09%	1.1624	1.1605 g./litre	99.83%
,,	,,	,,	1.2120	1.2075	99.64
0.4680	0.4673	99.85	1.9980	1.9970	99.94
0.7600	0.7572	99.64	,,	1.9992	100.08

TABLE V

Effect of iodine concentration.

	Thiocarbamide soln. taken	Iodine soln. used.	Thiocarbamide found.	
A.	0.4680 g.litre	0.0550 *N*	0.4672 g./litre	99.85%
	,,	0.08882	0.4668	99.77
B.	1.9980	0.0550	1.9976	99.86
	,,	0.09391	1.9860	99.40

Back-titrations of Excess Oxidant against Arsenious Oxide.—In certain experiments, a known (excess) volume of iodine solution was taken, to which was added a 10% sodium bicarbonate and a known volume of thiocarbamide solution. The excess iodine was titrated potentiometrically against a standard solution of arsenious oxide. The difference between the initial (blank) and final titre values of As_2O_3 corresponds to the iodine consumed, and therefore a direct determination of thiocarbamide can be achieved.

$$A_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI$$

or

$$CS(NH_2)_2 \equiv 8\,I \equiv 2\,As_2O_3.$$

The results of these experiments are represented in Table VI.

TABLE VI

S. No.	Thiocarbamide present.	Thiocarbamide found.	
1.	0.4680 g./litre	0.4692 g./litre	100.20 %
2.	,,	,,	,,
3.	,,	,,	,,
4.	1.2120	1.2145	,,
5.	,,	1.21136	99.95
6.	,,	,,	,,

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SEARCH FOR NEW ANTIMALARIALS. PART V. SYNTHESIS OF SOME 8-AMINOALKYLAMINO- AND 8-DIALKYLAMINOALKYLAMINO-CHROMONES

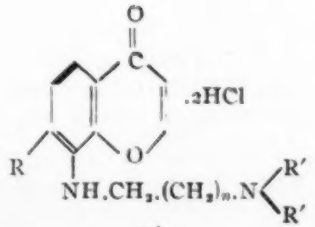
By A. B. Sen and P. R. Singh

Twentyfive 8-aminoalkylamino- and 8-dialkylaminoalkylamino-chromones have been synthesised as possible antimalarials.

In view of the antimalarials chloroquine and camoquine having proved to be effective amoebacidal agents (Conan, *Amer. J. Trop. Med.*, 1948, **28**, 107 ; Hoekenga *et al* , *ibid.*, 1950, **30**, 625), it was thought worthwhile to synthesise some compounds as antimalarials, based on the structure of certain potential amoebacides. Considering the high amoebacidal activity exhibited by the Mannich bases derived from substituted chromanones (2 : 3-dihydrochromones) (Wiley, *J. Amer. Chem. Soc.*, 1951, **73**, 4205), aminoalkylamino and dialkylaminoalkylamino side chains have been introduced in substituted chromones for studying their antimalarial activity.

In the present investigation, the required 7-substituted chromones were obtained by reacting ethyl formate with various 4-substituted-2-hydroxyacetophenones in ether in the cold, following the method of Späth and Lederer (*Ber.*, 1930, **63**, 743), modified by Joshi *et al.* (this *Journal*, 1959, **36**, 59). The 7-methoxychromone was also demethylated with anhydrous aluminium chloride to 7-hydroxychromone. These chromones, on nitration at 0°, yielded the 8-nitrochromones (Joshi *et al.*, *loc. cit.*) which, on reduction with iron powder and water in the presence of ferrous sulphate (Hodgson and Marsden, *J. Chem. Soc.*, 1944, 308), yielded the corresponding 8-aminochromones.

The 8-aminoalkylamino- and 8-dialkylaminoalkylamino-chromones were prepared by refluxing the 8-aminochromones with various amino- and dialkylamino-alkyl bromide-hydrobromides in dry benzene in the presence of an excess of anhydrous potassium carbonate and were isolated as dihydrochlorides in the usual way. The antimalarial activities of the compounds are under investigation at the Malaria Institute of India, Delhi.



(I)

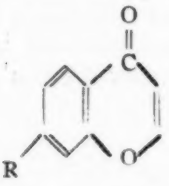
EXPERIMENTAL

4-Substituted 2-Hydroxyacetophenones.—Resacetophenone (Robinson and Shah, *ibid.*, 1934, 1491) was methylated to paeanol (4-methoxy-2-hydroxyacetophenone) (Crabtree and Robinson, *ibid.*, 1918, **113**, 868). 4-Ethoxy-2-hydroxyacetophenone was obtained in the same way by ethylation with ethyl iodide and KOH in methanol. 4-Methyl- and 4-ethyl-2-hydroxyacetophenones were prepared by the Fries rearrangement of *m*-cresyl acetate (Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56) and *m*-ethyl phenylacetate (Sen and Tiwari, this *Journal*, 1952, **29**, 357) respectively.

7-Substituted chromones were prepared by following the method described by Joshi *et al.* (*loc.cit.*). To a suspension of powdered sodium (0.3*M*) in dry ether (50 c.c.) a cold solution of the substituted *o*-hydroxyacetophenone (0.1*M*) in dry and freshly distilled ethyl formate (25 c.c.) was added in small lots with shaking. The reaction mixture was left for 4 hours in an ice-chest and then overnight at room temperature, after which the ethyl formate-ether mixture (1 : 10, 40 c.c.) was added and the whole refluxed for 1 hour on a water-bath. After cooling, water (100 c.c.) was added and the alkaline aqueous layer separated. It was strongly acidified with 50% H_2SO_4 and heated on a water-bath for 1 hour. On cooling and subsequent neutralisation with solid sodium bicarbonate, the chromone separated out as a solid, which was filtered, washed with 5% aqueous sodium carbonate and then with water, and finally recrystallised from petroleum ether (b.p. 60-80°).

The 7-methoxychromone was also demethylated to 7-hydroxychromone with anhydrous aluminium chloride. A solution of 7-methoxychromone (0.023*M*) in CS_2 was slowly added with stirring to a filtered solution of anhydrous aluminium chloride (0.048*M*) in CS_2. The crystalline addition product was filtered and dried in vacuum. It was refluxed in benzene solution for 3 hours. The semisolid mass obtained on cooling was separated from benzene and poured in water (15 c.c.). The 7-hydroxychromone separating was purified by dissolving it in hot benzene and reprecipitating with petroleum ether. The m.p., yield, etc. of these chromones are recorded in Table I.

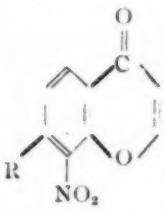
TABLE I



	Chromones.						Oximes.			
			% Carbon.		% Hydrogen.				% Nitrogen.	
R.	M.P.	Yield.	Found.	Calc.	Found.	Calc.	M.P.	Formula.	Found.	Calc.
OH	...	...	...	...	...	...	283°	$C_9H_7O_3N$	7.87	7.91
OMe	...	...	...	...	...	...	154°	$C_{10}H_9O_3N$	7.29	7.25
OEt	103°	49%	69.36	69.47	5.29	5.26	131-32°	$C_{11}H_{11}O_3N$	6.77	6.83
Me	66°	43	74.88	75.00	4.90	5.00	112°	$C_{10}H_9O_2N$	7.91	8.00
Et	53-54°	46	75.79	75.86	5.81	5.75	98-99°	$C_{11}H_{11}O_2N$	7.38	7.41

7-Substituted 8-Nitrochromones.—Nitration of 7-substituted chromones resulted in the formation of the corresponding 8-nitrochromone (Joshi *et al.*, *loc.cit.*). A mixture of H_2SO_4 (*d* 1.8, 4.2 c.c.) and HNO_3 (*d* 1.42, 1.4 c.c.) was slowly added with continuous stirring to a solution of the 7-substituted chromone (0.02*M*) in H_2SO_4 (*d* 1.8, 17.5 c.c.). The mixture was kept at 0° for 4 hours and then poured over crushed ice (100 g.). The nitrochromone separated as a yellow solid which was filtered and recrystallised from ethyl acetate or ethanol. These nitrochromones are recorded in Table II.

TABLE II



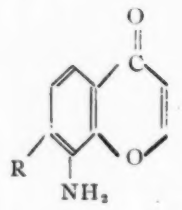
	Nitrochromones.				Oximes.			
			% Nitrogen.				% Nitrogen.	
R.	M.P.	Yield.	Found.	Calc.	M.P.	Formula.	Found.	Calc.
OH	...	...	...	...	291°	$C_9H_6O_5N_2$	12.48	12.61
OMe	...	...	...	...	267°	$C_{10}H_8O_5N_2$	11.85	11.86
OEt	219°	93%	5.87	5.96	271-72°	$C_{11}H_{10}O_5N_2$	11.26	11.20
Me	181°	96	6.81	6.83	204°	$C_{10}H_8O_4N_2$	12.77	12.73
Et	163°	88	6.28	6.39	211-13°	$C_{11}H_{10}O_4N_2$	11.93	11.97

Oximes of the various chromones and nitrochromones, prepared in the usual way, are recorded in Table I and Table II respectively.

7-Substituted 8-aminochromones were obtained by the reduction of the above nitrochromones with iron powder and water in presence of ferrous sulphate (Hodgson and Marsden, *loc.cit.*). A mixture of the substituted 8-nitrochromone (0.02*M*), iron powder (10 g.) and ferrous sulphate (1 g.) was refluxed in water (100 c.c.) for 1 hour; ammonia (*d* 0.88, 1 c.c.) was added to precipitate iron and the solution was filtered. The aminochromone separated as fine needles on passing CO_2 in the filtrate and subsequent concentration and cooling.

The aminochromones and their oximes and *N*-acetyl derivatives, prepared in the usual way, are recorded in Table III.

TABLE III



Aminochromones					Oximes.				N-Acetyl derivatives.			
			% Nitrogen.				% Nitrogen.				% Nitrogen.	
R.	M.P.	Yield.	Found.	Calc.	M.P.	Formula.	Found.	Calc.	M.P.	Formula.	Found.	Calc.
OH	199°	41	8.39%	8.38	229-30°	$C_9H_8O_3N_2$	13.99	14.06	257-58°	$C_{11}H_9O_4N$	6.36	6.39
OMe	167°	53	7.30	7.33	189-91°	$C_{10}H_{10}O_3N_2$	13.51	13.59	233°	$C_{12}H_{11}O_4N$	6.12	6.01
OEt	161-62°	38	6.77	6.83	180-82°	$C_{11}H_{12}O_3N_2$	12.68	12.73	245°	$C_{13}H_{13}O_4N$	5.65	5.67
Me	130-31°	47	7.89	8.00	165-66°	$C_{10}H_{10}O_2N_2$	14.70	14.74	178-79°	$C_{12}H_{11}O_3N$	6.39	6.45
Et	117-19°	40	7.33	7.41	152-54°	$C_{11}H_{12}O_2N_2$	13.69	13.73	159-60	$C_{13}H_{13}O_3N$	6.05	6.06

TABLE IV

Chromone dihydrochlorides.					Oximes.				Dipicrates			
			% Nitrogen.				% Nitrogen.				% Nitrogen.	
R.	M.P.	Yield.	Found.	Calc.	M.P.	Formula.	Found.	Calc.	M.P.	Formula.	Found.	Calc.
OH	199°	41	8.39%	8.38	229-30°	$C_9H_8O_3N_2$	13.99	14.06	257-58°	$C_{11}H_9O_4N$	6.36	6.39
OMe	167°	53	7.30	7.33	189-91°	$C_{10}H_{10}O_3N_2$	13.51	13.59	233°	$C_{12}H_{11}O_4N$	6.12	6.01
OEt	161-62°	38	6.77	6.83	180-82°	$C_{11}H_{12}O_3N_2$	12.68	12.73	245°	$C_{13}H_{13}O_4N$	5.65	5.67
Me	130-31°	47	7.89	8.00	165-66°	$C_{10}H_{10}O_2N_2$	14.70	14.74	178-79°	$C_{12}H_{11}O_3N$	6.39	6.45
Et	117-19°	40	7.33	7.41	152-54°	$C_{11}H_{12}O_2N_2$	13.69	13.73	159-60	$C_{13}H_{13}O_3N$	6.05	6.06

TABLE IV

Chromone dihydrochlorides.					Oximes.				Dipicrates			
			% Nitrogen.				% Nitrogen				% Nitrogen.	
	M.P.	Yield.	Found.	Calc.	M.P.	Formula.	Found.	Calc.	M.P.	Formula.	Found.	Calc.
						R′ = H; n=1.						
OH	280°	61%	9.51	9.56	168-69°	$C_{11}H_{13}O_3N_3$	17.84	17.87	202°	$C_{23}H_{18}O_{17}N_8$	16.47	16.52
OMe	297-98°	76	8.98	9.12	157-58°	$C_{12}H_{15}O_3N_3$	16.89	16.86	178-79°	$C_{24}H_{20}O_{17}N_8$	17 71	17.72
OEt	276-77°	70	8.70	8.72	153°	$C_{13}H_{17}O_3N_3$	16.03	15.96	181°	$C_{25}H_{22}O_{17}N_8$	15.81	15.86
Me	201°	69	9.67	9.62	141°	$C_{12}H_{15}O_2N_3$	17.99	18.02	160-61°	$C_{24}H_{20}O_{16}N_8$	16.48	16.57
Et	189-90°	57	9.18	9.15	132-33°	$C_{13}H_{17}O_2N_3$	16.87	17.00	152-53	$C_{25}H_{22}O_{16}N_8$	16.20	16.23
						R′ = Et; n=1.						
OH	251-52°	52	7.07	8.02	156-57°	$C_{15}H_{21}O_4N_3$	14.42	14.43	177°	$C_{27}H_{26}O_{17}N_8$	16.18	16.26
OMe	273-74°	61	7.68	7.71	154°	$C_{16}H_{23}O_3N_3$	13.59	13.77	165-66°	$C_{28}H_{28}O_{17}N_8$	14.99	14.97
OEt	243°	65	7.37	7.43	147-48°	$C_{17}H_{25}O_3N_3$	13.06	13.17	141-42°	$C_{29}H_{30}O_{17}N_8$	14.63	14.70
Me	221-22°	64	8.02	8.07	122-23°	$C_{16}H_{23}O_2N_3$	14.58	14.53	128°	$C_{28}H_{28}O_{16}N_8$	15.25	15.30
Et	167-68°	70	7.70	7.76	109-11°	$C_{17}H_{25}O_2N_3$	13.79	13.86	137°	$C_{29}H_{30}O_{16}N_8$	14.88	15.01
						R′ = Pr°; n=1.						
OH	249.50°	57	7.44	7.43	147-48°	$C_{17}H_{25}O_3N_3$	13.14	13.17	157°	$C_{29}H_{30}O_{17}N_8$	14.62	14.70
OMe	263°	64	7.06	7.16	131-32°	$C_{18}H_{27}O_3N_3$	12.57	12.61	138-39°	$C_{30}H_{32}O_{17}N_8$	14.37	14.43
OEt	267°	53	6.88	6.91	141-42°	$C_{19}H_{29}O_3N_3$	12.03	12.10	161-62°	$C_{31}H_{34}O_{17}N_8$	14.07	14.18
Me	209°	49	7.43	7.47	117°	$C_{18}H_{27}O_2N_3$	13.22	13.25	153°	$C_{30}H_{30}O_{16}N_8$	14.71	14.74
Et	199-200°	51	7.15	7.20	103-104°	$C_{19}H_{29}O_2N_3$	12.67	12.69	129-30°	$C_{31}H_{31}O_{16}N_8$	14.45	14.47
						R′ = Et; n=3.						
OH	224-25°	49	7.33	7.43	119-20°	$C_{17}H_{25}O_3N_3$	13.09	13.17	156-57°	$C_{29}H_{30}O_{17}N_8$	14.71	14.70
OMe	209-10°	58	7.11	7.16	100-101°	$C_{18}H_{27}O_3N_3$	12.55	12.61	137°	$C_{30}H_{32}O_{17}N_8$	14.40	14.43
OEt	177°	60	6.88	6.91	109°	$C_{19}H_{29}O_3N_3$	12.18	12.10	122 23°	$C_{31}H_{34}O_{17}N_8$	14.03	14.18
Me	146°	45	7.46	7.47	89-90°	$C_{18}H_{27}O_2N_3$	13.17	13.25	126°	$C_{30}H_{32}O_{16}N_8$	14.79	14.74
Et	131-32°	52	7.19	7.20	78°	$C_{19}H_{29}O_2N_3$	12.65	12.69	128-29°	$C_{31}H_{34}O_{16}N_8$	14.42	14.47
						R′ = Pr°; n=3.						
OH	227°	59	6.98	6.91	101-103°	$C_{19}H_{29}O_3N_3$	11.96	12.10	144°	$C_{31}H_{31}O_{17}N_8$	14.20	14.18
OMe	202-204°	60	6.67	6.68	76°	$C_{20}H_{31}O_3N_3$	11.60	11.63	127-28°	$C_{32}H_{36}O_{17}N_6$	13 88	13.93
OEt	122-23°	53	6.44	6.47	81-82°	$C_{21}H_{33}O_3N_3$	11.12	11.20	136-37°	$C_{33}H_{38}O_{17}N_8$	13.39	13.41
Me	118-19°	46	6.92	6.95	63°	$C_{20}H_{31}O_2N_3$	11.99	12.17	128°	$C_{32}H_{36}O_{16}N_8$	14.17	14.21
Et	109-11°	48	6.68	6.72	46°	$C_{21}H_{33}O_2N_3$	11.63	11.70	131°	$C_{33}H_{38}O_{16}N$	13.84	13.96

δ-Dipropyl^{n}aminobutyl bromide-hydrobromide was prepared by distilling δ-dipropyl^n aminobutanol with 48% hydrobromic acid, following the method of Cortese (*J. Amer. Chem. Soc.*, 1936, **58**, 191), m.p. 93°, yield 53%. (Found: N, 4.47; Br, 50.41. $C_{10}H_{23}NBr_2$ requires N, 4.42; Br, 50.47%).

δ-Dipropyl^n aminobutanol required for the above reaction was prepared from tetramethylenechlorohydrin (Kirner and Richter, *ibid.*, 1929, **51**, 2503) (0.1*M*) and dipropyl^n-amine (0.13*M*) by a similar procedure as described by Burnett *et al.* (*ibid.*, 1937, **59**, 2248); b.p. 66-69°/12 mm, yield 61%. (Found: N, 7.93. $C_{10}H_{23}ON$ requires N, 8.09%).

δ-Diethylaminobutyl bromide-hydrobromide was similarly obtained from tetramethylenechlorohydrin and diethylamine, m.p. 117°, yield 67%. (Found: N, 4.81; Br, 55.27. $C_8H_{19}NBr_2$ requires N, 4.84; Br, 55.36%).

β-Dipropyl^n aminoethyl bromide-hydrobromide, β-diethylamino ethyl bromide-hydrobromide and β-aminoethyl bromide-hydrobromide were prepared in the same way by the known methods (Amundsen and Krantz, *ibid.*, 1941, **63**, 305; Cortese, *loc. cit.*).

8-Aminoalkylamino- and *8-dialkylaminoalkylamino-chromones* were obtained by refluxing the 8-aminochromones (0.05*M*) with various amino- and dialkylamino alkyl bromide-hydrobromides (0.05*M*) and anhydrous potassium carbonate (0.11*M*) in dry benzene for 5 hours, removing the solvent and extracting the residue with ether. Base dihydrochlorides were prepared by passing HCl gas into the dried ether extract and then recrystallised from 75% ethanol.

The oximes and the dipicrates of the bases were prepared by the usual procedures. The m.p., yield, analysis, etc. of the dihydrochlorides, oximes and dipicrates of the bases are recorded in Table IV.

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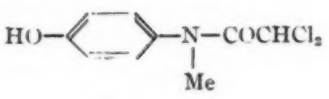
POSSIBLE ANTAMOEBIC AGENTS. PART XI. SYNTHESIS OF COMPOUNDS ANALOGOUS TO ENTAMIDE

By A. B. Sen and O. P. Madan

Several substituted dichloroacetanilides have been synthesised from subsituted *N*-alkylanilines with a view to testing them for their antamoebic activity.

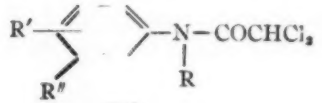
Recently Boots Pure Drug Co. have introduced a new synthetic amoebacide, Entamide (2 : 2-dichloro-4′-hydroxy-*N*-methylacetanilide). Its action on *E. histolytica* is specific ; it is non-toxic, inexpensive and the treatment with it is convenient as no bed rest is required. Bristow *et al.* (*Trans. Roy. Soc. Trop. Med. Hyg.*, 1956, **50**, 182) and Woodruff (*Brit. Med. J.*, 1956, **1**, 288) described it to be very useful for such patients who were symptomless cyst passers.

The present work reports the synthesis of eleven substituted dichloroacetanilides (II) from the corresponding *N*-alkylanilines having different substituents (hydroxy, methoxy, chloro, iodo and methyl) in the nucleus and different alkyl radicals (ethyl, propyl^{n} and butyl^{n}) at the nitrogen atom, with a view to studying their antamoebic activity.



(I)

(Entamide)



(II)

{ R′ and R″ = substituents in the nucleus.
R = substituent at nitrogen atom.

3-Chloro-4-hydroxy-*N*-alkylanilines were prepared by refluxing 2-chloro 4-aminophenol and different alkyl halides in absolute alcohol in the presence of calcined potassium carbonate. 3-Chloro-4-methoxy-*N*-alkylanilines were obtained by the reductive alkylation of 2-chloro 4-nitroanisole, following the method of Emerson and Mohrman (*J. Amer. Chem. Soc.*, 1940, **62**, 69) using acetaldehyde, acetone and butyr^{n}aldehyde. 2-Methyl-4-iodo-*N*-alkylanilines were obtained similarly from 2-methyl 4-iodoaniline, acetone and butyr^{n}aldehyde.

Dichloroacetanilides have been synthesised from 3-chloro-4-hydroxy-, 3-chloro-4-methoxy- and 2-methyl-4-iodo-anilines, 3-chloro-4-hydroxy- and 3-chloro-4-methoxy- and 2-methyl-4-iodo-*N*-alkylanilines by the action of dichloroacetyl chloride (in dichloroethane) following the method of Surrey (*J. Amer. Chem. Soc.*, 1954, **76**, 2216).

EXPERIMENTAL

3-Chloro-4-hydroxy-N-alkylanilines.—The starting material for this was 2-chloro-4-nitrophenol which was prepared from *p*-nitrophenol according to Christiansen (*ibid.*, 1923, **45**, 2192). This was easily reduced to *o*-chloro-*p*-aminophenol with sodium hydrosulphite. (Reduction with zinc dust and NaOH or Fe and HCl was not found to be satisfactory). Attempts made for the synthesis of *o*-chloro-*p*-methylaminophenol and its sulphate (cf. Christiansen, *loc. cit.*) did not succeed. Hence, a large number of other methods were tried for the *N*-alkylation of *o*-chloro-*p*-aminophenol, most of which were unsuccessful.

Finally 2-chloro-4-*N*-ethylamino-, -propyl^{i}amino- and -butyl^{n}amino-phenols were obtained by refluxing 2-chloro-4-aminophenol with appropriate alkyl bromide or iodide accompanied with calcined potassium carbonate for 8 to 12 hours.

2-Chloro-4-N-ethylaminophenol.—*o*-Chloro-*p*-aminophenol (4.3 g., 0.03 *M*), ethyl iodide (4.7 g., 0.03*M*) and calcined potassium carbonate (2.1 g., 0.015 *M*) were refluxed in absolute alcohol (30 c.c.) for 8 hours on a water-bath. Potassium iodide formed was filtered off, alcohol removed under reduced pressure and the residue was taken up in ether. The ether extract was washed with water, dried over anhydrous magnesium sulphate and finally the ether was removed. The residue was distilled under reduced pressure when the phenol was obtained as a liquid, b.p. 172°/16 mm, which soon solidified and yielded a compound of m.p. 63-64°, yield 2.6 g. (51%). (Found : C, 53.76 ; H, 5.44 ; N, 7.92. $C_8H_{10}ONCl$ requires C, 55.97 ; H, 5.83 ; N, 8.16%).

2-Chloro-4-N-propyl^{i}aminophenol.—*o*-Chloro-*p*-aminophenol (0.03 *M*), propyl^{i} iodide (0.03 *M*) and calcined K_2CO_3 (0.015 *M*) were heated in absolute alcohol for 10 hours. 2-Chloro-4-*N*-propyl^{i}aminophenol was obtained in the usual way, m.p. 107°, yield 50% of the theory. (Found : N, 7.39. $C_9H_{12}ONCl$ requires N, 7.54%).

2-Chloro-4-N-butyl^{n}aminophenol was obtained in the same way by refluxing *o*-chloro-*p*-aminophenol (4.3 g., 0.03 *M*) and butyl^{n} bromide (4.1 g., 0.03*M*) in absolute alcohol for 12 hours ; b.p. 208°/6 mm, yield 3.0 g. (53%). (Found : N, 6.85. $C_{10}H_{14}ONCl$ requires N, 7.01%).

3-Chloro-4-methoxy-N-alkylanilines.—*o*-Chloro-*p*-nitroanisole was prepared from *o*-chloro-*p*-nitrophenol, following the method of Hodgson and Handlay (*J. Chem. Soc.*, 1926, 543). 2-Chloro-4-*N*-ethylamino-, -propyl^{i}amino- and -butyl^{n}amino-anisoles were obtained from *o*-chloro-*p*-nitroanisole, following the method of Emerson and Mohrman (*loc. cit.*).

2-Chloro-4-N-butyl^{n}aminoanisole.—*o*-Chloro-*p*-nitroanisole (3.75 g., 0.02 *M*), butyr^{n}-aldehyde (5.16 g., 0.06*M*), sodium acetate (0.4 g.) and absolute alcohol (35 c.c.) were refluxed for 1 hour. The mixture was then reduced catalytically using Raney nickel till no more of hydrogen was absorbed. On releasing the pressure, the mixture was removed from hydrogenation bottle. Raney nickel was filtered off and 2-chloro-4-*N*-

butyl^n-aminoanisole was obtained in the usual way as a yellow liquid, b.p. 188°/5 mm, yield 5.8 g. (75%). (Found : N, 6.50. $C_{11}H_{16}ONCl$ requires N 6.55%).

2-*Chloro*-4-*N*-*ethylaminoanisole*.— *o*-Chloro-*p*-nitroanisole (2.34 g., 0.0125 *M*), acetaldehyde (5.5 g., 0.0125 *M*) and sodium acetate (0.2 g.) in absolute alcohol were directly reduced catalytically. The anisole was obtained in the usual way as a thick red liquid, b.p. 165°/5 mm, yield 2.1 g. (77%). (Found : N, 7.76. $C_9H_{12}ONCl$ requires N, 7.74%).

2-*Chloro*-4-*N*-*propyl*^{i}*aminoanisole* was obtained similarly from *o*-chloro-*p*-nitroanisole (3.75 g., 0.02*M*), acetone (4.64 g., 0.08*M*) and sodium acetate (0.2 g.) as a brownish yellow liquid, b.p. 132°/5 mm, yield 2.6 g. (54%). (Found : N, 6.82. $C_{10}H_{14}ONCl$ requires N, 7.01%).

The *picrate* was prepared in absolute alcohol in the usual way, m.p. 172°. (Found : N, 13.01. $C_{16}H_{17}O_8N_4Cl$ requires N, 13.06%).

2-*Methyl*-4-*iodo*-*N*-*alkylanilines*.—2-Methyl-4-iodo-*N*-propyl^{i}aniline and 2-methyl-4-iodo-*N*-butyl^{n}aniline were prepared from 5-iodo-2-aminotoluene by the method of Emerson and Mohrman (*loc. cit.*).

2 *Methyl*-4-*iodo*-*N*-*propyl*^{i}*aniline*.—5-Iodo-2-aminotoluene (4.78 g., 002 *M*), dry acetone (4.64 g., 0.08 *M*), sodium acetate (0.4 g.) and absolute alcohol were heated on a water-bath for 1 hour and then reduced catalytically. The aniline derivative was obtained as a yellow liquid, b.p. 122°/6 mm, yield 2.7 g. (47 %). (Found : N, 5.18. $C_{10}H_{14}NI$ requires N, 5.09%).

2-*Methyl*-4-*iodo*-*N*-*butyl*^{n}*aniline* was obtained similarly from 5-iodo-2-aminotoluene (2.33 g., 0.01 *M*) and butyr^{n}aldehyde (1.44 g., 0.02 *M*) with sodium acetate and absolute alcohol as a light yellow liquid, b.p. 135-36°/5 mm, yield 1.0 g. (35%). (Found : N, 4.51. $C_{11}H_{16}NI$ requires N, 4.87%).

The *picrate* was prepared in the usual way in alcohol, m.p. 140°. (Found : N, 10.27. $C_{17}H_{19}O_7N_4I$ requires N, 10.81%).

Dichloroacetanilides were prepared from 3-chloro-4-hydroxyaniline, 3-chloro-4-methoxyaniline, 2 methyl-4-iodoaniline and from the corresponding *N*-alkylanilines mentioned above, following the method of Surrey (*loc. cit.*). Dichloroacetyl chloride (0.005 *M*) in dichloroethane (5 c.c.) was added gradually with stirring to a mixture of substituted aniline (0.005 *M*) in dichloroethane (15 c.c.) and 1*N*-NaOH (5 c.c.). The temperature was kept between 0° and -5° by external cooling. The reaction mixture was stirred and was kept at room temperature overnight. Organic layer was separated, washed successively with 1 *N*-NaOH, water, 1 *N*-HCl and water. The dichloroethane extract was then dried over K_2CO_3 (calcined). The dichloroacetanilides were obtained after removing dichloroethane and were recrystallised from suitable solvents as required or purified by distilling under reduced pressure.

The m.p., b.p., yield, analysis etc. of dichloroacetanilides are recorded in Table I.

TABLE I

R.	M.P. or B.P.	Yield.	Formula.	% Nitrogen. Found.	Calc.
		R′ & R″ = 3-chloro-4-hydroxy.			
H	133°	88%	$C_8H_6O_2NCl_3$	5·35	5·50
Et	176°	23	$C_{10}H_{10}O_2NCl_3$	4·90	4·95
Pr^i	175°/5 mm	45	$C_{11}H_{12}O_2NCl_3$	4·38	4·72
Bu^n	129°/5	47	$C_{12}H_{14}O_2NCl_3$	4·69	4·50
		R′ & R″ = 3-chloro-4-methoxy.			
H	124°	75	$C_9H_8O_2NCl_3$	5·03	5·21
Et	105°/5	46	$C_{11}H_{12}O_2NCl_3$	4·6₀	4·72
Pr^i	113°	65	$C_{12}H_{14}O_2NCl_3$	4·38	4·50
Bu^n	133°/5	50	$C_{13}H_{16}O_2NCl_3$	4·20	4·31
		R′ & R″ = 2-methyl-4-iodo.			
H	190°	79	$C_9H_8ONCl_2I$	4·05	4·07
Pr^i	134°	78	$C_{12}H_{14}ONCl_2I$	3·89	3·62
Bu^n	61°	51	$C_{13}H_{16}ONCl_2I$	3·39	3·50

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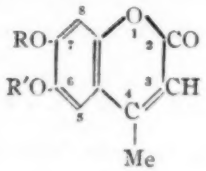
STUDIES ON 6:7-DIHYDROXY-4-METHYLCOUMARIN AND ITS METHYL ETHERS

By M. G. Patel and Suresh Sethna

6 : 7-Dihydroxy-4-methylcoumarin and its dimethyl ether, on bromination with one mole of bromine, furnish the 3-bromo compound, and wtih two moles of bromine, the 3 : 8-dibromo compound. The 7-methoxy derivative, however, affords the 3 : 5-dibromo compound with two moles of bromine. In nitration, the 7-methoxy derivative yields the 5-nitro derivative whereas the 6 : 7-dimethoxy derivative furnishes the 3-nitro derivative.

Considerable work has been done on the reactivity of various mono- and dihydroxy-coumarins, but the data regarding the reactivity of 6 : 7-dihydroxycoumarins are meagre. 6:7-Dihydroxycoumarin derivatives occur in nature and are therefore of interest. King *et al.* (*J. Chem. Soc.*, 1954, 1392) and Gurbaksh Singh *et al.* (*Chem. & Ind.*, 1954, 1294) as a part of their studies on certain plant products brominated 6:7-dimethoxycoumarin and obtained the 3-bromo compound. Späth and Dobrovonly (*Ber.*, 1938, **71B**, 1831) nitrated 6:7-dimethoxy- and 6-methoxy-7-hydroxy-coumarins and obtained the 3-nitro compound. The present work deals with the systematic study of the pattern of substitution in the more readily accessible 6:7-dihydroxy-4-methylcoumarin (Ia) and its 7-methoxy (Ib) and 6:7-dimethoxy (Ic) derivatives.



(I)

[(a) R=R'=H. (b) R=Me ; R'=H. (c) R=R'=Me]

(Ia) on bromination with one mole of bromine afforded the 3-bromo derivative, the dimethyl ether of which furnished a coumarilic acid derivative on treatment with alkali. With two moles of bromine, the 3 : 8-dibromo compound was obtained, as seen by a direct comparison of its dimethyl ether with an authentic specimen, synthesised as follows :

7-Hydroxy-8-bromo-4-methylcoumarin, obtained by the Pechmann condensation of 2-bromoresorcinol with ethyl acetoacetate, on methylation and the Elbs persulphate oxidation, yielded 6-hydroxy-7-methoxy-8-bromo-4-methylcoumarin. This on bromination and methylation afforded 6 : 7-dimethoxy-3 : 8-dibromo-4-methylcoumarin, which on boiling with alkali furnished a bromocoumarilic acid. (Ib) afforded with one mole of bromine the 3-bromo product, but with two moles, a dibromo product was obtained, the methyl ether of which furnished a bromocoumarilic acid. As the dibromo

compound is different from the 3:8-dibromo product, described above, it must be the 3:5-dibromo derivative. (Ic) yielded the 3-bromo and the 3:8-dibromo derivatives when brominated with one and two moles of bromine respectively.

Iodination of (Ia), (Ib) and (Ic) with iodine and iodic acid, iodine and ammonia, and iodine monochloride under varying conditions did not succeed. With iodine monochloride (Ib) furnished a chloro compound which has not been investigated.

(Ia) on nitration gave rise to an unworkable mass from which no pure product could be obtained. (Ib), however, afforded a compound different from 7-methoxy-6-hydroxy-8-nitro-4-methylcoumarin, synthesised by the Elbs persulphate oxidation of 7-methoxy-8-nitro-4-methylcoumarin. It remained unchanged on heating with liquor ammonia. It is therefore 7-methoxy-6-hydroxy-5-nitro-4-methylcoumarin. On demethylation, the nitro group was eliminated and 6:7-dihydroxy-4-methylcoumarin was obtained. (Ic) on nitration yielded the 3-nitro compound which on reaction with liquor ammonia furnished 2-hydroxy-4:5-dimethoxyacetophenone. The nitro compound was reduced to the 3-amino compound and also demethylated to 6:7-dihydroxy-3-nitro-4-methylcoumarin.

The Friedel-Crafts acetylation of (Ia) and (Ib) and the Fries migration of 6:7-diacetoxy 4-methylcoumarin did not succeed, only (Ia) was obtained. 7-Methoxy-6-acetoxy-4-methylcoumarin on the Fries reaction at 120-30° furnished (Ia) and at lower temperatures, (Ib). Seshadri *et al.* (*J. Chem. Soc*, 1954, 3065) have obtained 6:7-dihydroxy-8-acetyl-4-methylcoumarin by the Elbs persulphate oxidation of 7-methoxy-8-acetyl-4-methylcoumarin. It may be mentioned here that when direct substitution in 8-position is not possible, the Elbs persulphate oxidation of 7-methoxy-8-substituted coumarins offers a convenient method for the synthesis of 8-substituted 6:7-dihydroxy-coumarins.

*Experimental

Bromination.—To the coumarin derivative (2 g.), dissolved in a minimum quantity of glacial acetic acid, the required quantity of bromine solution (10% in acetic acid) was added dropwise; after 4 hours the product, which separated or was obtained by dilution with water, was washed with dilute acetic acid and then crystallised from either acetic acid or ethanol.

Methylation.—The methyl ethers were prepared by refluxing the acetone solutions of the compounds with dimethyl sulphate in the presence of anhydrous potassium carbonate and crystallised from acetic acid or alcohol. In the methylation of 7-methoxy-6-hydroxy-3:5-dibromo-4 methylcoumarin, benzene was used as the solvent as it was found to decompose in acetone solution.

7-Hydroxy-8-bromo-4-methylcoumarin.—To a mixture of 2-bromoresorcinol (1.9 g.) and ethyl acetoacetate (1.6 c.c.), 80% H_2SO_4 (10 c.c.) was added with external cooling. The solid separating on pouring the reaction mixture next day on crushed ice was crystallised from acetic acid in needles, m.p. 255-57°, yield 1.9 g. (Found: Br, 31.3. $C_{10}H_7O_3Br$ requires Br, 31.4%).

*All melting points are uncorrected.

The *methyl ether* was crystallised from alcohol in needles, m.p. 206-208°. (Found : Br, 30.0. $C_{11}H_9O_3Br$ requires Br, 29.7%).

6 *Hydroxy-7-methoxy-8-bromo-4-methylcoumarin.*—The above methyl ether (2.7 g.) was dissolved in 10% NaOH (30 c.c.) by warming on a steam-bath. It was then oxidised with potassium persulphate (3 g. in 60 c.c. of distilled water) according to Parikh and Sethna (this *Journal*, 1950, **27**, 364). The product obtained was crystallised from dilute ethanol in needles, m.p. 220-21°. (Found : Br, 28.2. $C_{11}H_9O_4Br$ requires Br, 28.1%).

6-Hydroxy-7-methoxy-3 : 8-dibromo-4-methylcoumarin.—To the above coumarin (2.8 g.), dissolved in minimum quantity of acetic acid, bromine (1.6 g.) in acetic acid (16 c.c.) was added. The product, which separated on keeping at room temperature for 2 hours, was crystallised from ethanol as yellow needles (2.8 g.), m.p. 257-58°. (Found : Br, 44.4. $C_{11}H_8O_4Br_2$ requires Br, 43.9%).

The *methyl ether* has been described in Table I.

TABLE I

Products obtained on bromination.

No	Substance.	Products obtained.	M P.	Formula.	% Bromine. Found.	% Bromine. Calc.	Completely methylated products of the bromo compounds shown in column 3.
1.	6 : 7-Dimethoxy-M	6 : 7-Dimethoxy-3-bromo-M	205-206°	$C_{12}H_{11}O_4Br$	26.4	26.7	...
2.	,,	6 : 7-Dimethoxy-3 : 8-dibromo-M	215-16°	$C_{12}H_{10}O_4Br_2$	42.8	42.3	...
3.	7-Methoxy-6-hydroxy-M	7-Methoxy-6-hydroxy-3-bromo-M	237-38°	$C_{11}H_9O_4Br$	28.6	28.1	a
4.	,,	7-Methoxy-6-hydroxy-3 : 5-dibromo-M *	200°	$C_{11}H_8O_4Br_2$	44.3	44.0	b
5.	6 : 7-Dihydroxy-M	6 : 7-Dihydroxy-3-bromo-M	244-45°	$C_{10}H_7O_4Br$	30.1	29.5	c
6.	,,	6 : 7-Dihydroxy-3 : 8-dibromo-M	267-68°	$C_{10}H_6O_4Br_2$	45.1	45.7	d

a. Methyl ether same as 1 (column 3).

b. Methyl ether, m.p. 195°. (Found : Br, 43.00. $C_{12}H_{11}O_4Br_2$ requires Br, 42.3%).

c. Methyl ether same as 1 (column 3).

d. Methyl ether same as 2 (column 3).

*. Obtained on heating the parent compound with 4 mols. of bromine in acetic acid on a steam-bath for 4 hours. Product crystallised from alcohol in needles.

M denotes -4-methylcoumarin (columns 2 and 3).

5 : 6-Dimethoxy-3-methylcoumarilic Acid.—6 : 7-Dimethoxy-3-bromo-4-methylcoumarin (0.5 g.) was refluxed with alcoholic potash (25 c.c., 10%) for 2 hours on a steam-bath. The product, obtained on acidification of the diluted solution, was purified through sodium bicarbonate solution. It was crystallised from acetic acid in thin plates, m.p. 220°. (Found : C, 61.4 ; H, 5.3. $C_{12}H_{12}O_5$ requires C, 61.0 ; H, 5.1%). It developed a violet coloration with H_2SO_4 (conc).

5:6-*Dimethoxy*-7-*bromo*-3-*methylcoumarilic acid* was obtained from 6:7-dimethoxy-3:8-dibromo-4-methylcoumarin as above. It was crystallised from acetic acid in needles, m.p. 270-72°. (Found: Br, 25.5. $C_{12}H_{11}O_5Br$ requires Br, 25.4%). It developed a violet coloration with H_2SO_4 (warm, conc.).

5:6-*Dimethoxy*-4-*bromo*-3-*methylcoumarilic acid* was obtained from 6:7-dimethoxy-3:5-dibromo-4-methylcoumarin as above and crystallised from acetic acid in white needles, m.p. 240-44° (decomp.). (Found: Br, 25.2. $C_{12}H_{11}O_5Br$ requires Br, 25.4%). It showed a greenish coloration with H_2SO_4 (warm, conc.).

6-*Hydroxy*-7-*methoxy*-8-*nitro*-4-*methylcoumarin*.—7-Methoxy-8 nitro-4-methylcoumarin (1 g.) was oxidised with potassium persulphate as usual. The product obtained was crystallised from dilute alcohol in needles, m.p. 255-56° (decomp.). (Found: N, 5.6. $C_{11}H_9O_6N$ requires N, 5.6%).

6:7-*Dimethoxy*-3-*nitro*-4-*methylcoumarin*.—6:7-Dimethoxy-4-methylcoumarin (2.2 g.) was dissolved in acetic acid and a mixture of nitric acid (2 c.c.) and acetic acid (6 c.c.) was added dropwise at room temperature with stirring. Bright yellow needles separated after stirring for some time. The reaction mixture was poured on crushed ice and filtered. The product obtained was crystallised from acetic acid in bright yellow needles, m.p. 215-17°. (Found: N, 4.9. $C_{12}H_{11}O_6N$ requires N, 5.2%).

The above 3-nitrocoumarin (1 g.) was boiled with liquor ammonia (60 c.c.) for 2½ hours on a steam-bath; the solution obtained on acidification was extracted with ether and the residue obtained after removal of ether was extracted with benzene. The product obtained on removal of benzene was crystallised from water, m.p. 112-14°. Mixed m.p. with 2-hydroxy-4:5-dimethoxyacetophenone, prepared according to Bargellini and Aureli (*Atti R. Accad. Lincei*, 1911, *v*, **20**, 118) was not depressed.

6:7-*Dimethoxy*-3-*amino*-4-*methylcoumarin*.—To 6:7-dimethoxy-3-nitro-4-methylcoumarin (2.6 g.) and stannous chloride (14 g.), HCl (conc., 100 c.c.) was added and the reaction mixture heated under reflux for 3 hours. It was made alkaline with ammonia and repeatedly extracted with ether. The pale yellow solid obtained on removal of ether was crystallised from benzene-petroleum ether in silky needles (1.3 g.), m.p. 164-65°. (Found: N, 5.6. $C_{12}H_{13}O_4N$ requires N, 6.0%).

6:7-*Dihydroxy*-3-*nitro*-4-*methylcoumarin*.—6:7-Dimethoxy-3-nitro-4-methylcoumarin was demethylated with hydriodic acid in acetic anhydride. The product obtained was crystallised from very dilute alcohol in thin plates, m.p. 229-30°. (Found: N, 6.0. $C_{10}H_7O_6N$ requires N, 5.9%).

6-*Hydroxy*-7-*methoxy*-5-*nitro*-4-*methylcoumarin*.—7-Methoxy-6-hydroxy-4 methylcoumarin (2.06 g.) was suspended in acetic acid (40 c.c.) and a mixture of fuming nitric acid (2 c.c.) and acetic acid (6 c.c.) was added dropwise at room temperature with stirring. The product separating was crystallised from alcohol in thin plates, m.p. 220-22° (decomp.). (Found: N, 5.2. $C_{11}H_9O_6N$ requires N, 5.6%).

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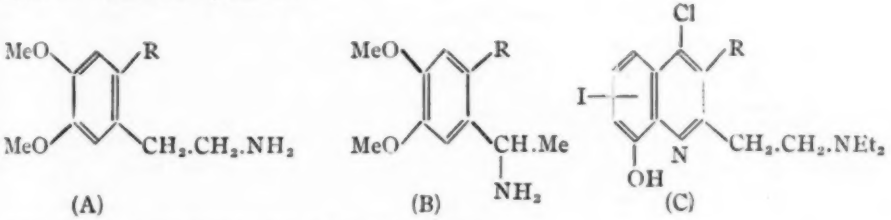
SEARCH FOR NEW AMOEBACIDES. PART IV

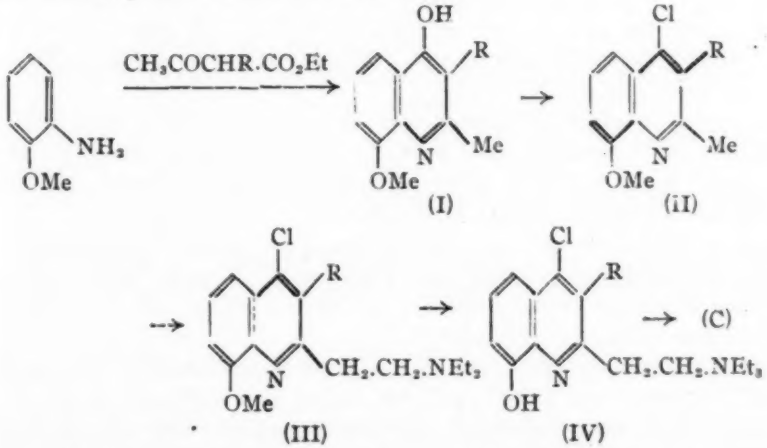
By K. L. Pathak and B. Pathak

Syntheses of 2-β-diethylaminoethyl-3-alkyl-4-chloro-5- or -7-iodo-8-hydroxyquinolines have been effected having alkyl substitution of Me, Et, Pr^n, Bu^n and amyl^n groups with the object of observing their amoebacidal activity.

Some halo-8-hydroxyquinolines, like chinifon, vioform and diodoquine, possess pronounced amoebacidal activity. Burckhalter and Edgerton (*J. Amer. Chem. Soc.*, 1951, **73**, 4837) observed high *in vitro* amoebacidal activity in 5-chloro-7-diethylaminomethyl-8-quinolinol. Koushiva (*J. Sci. Ind. Res.*, 1957, **16C**, 224) observed high *in vitro* amoebacidal activity existing among compounds of the types A and B, where R = Bu^n or $C_6H_{13}{}^n$. In view of these observations it has been considered worthwhile to synthesise and investigate amoebacidal activity in compounds of the type C. These compounds:



have been synthesised by the following route:



Yields of compounds of type (I) gradually decrease with the increase of carbon atom in the alkyl group. Iodination of compounds (IV) has been attempted with

different iodinating agents, like a solution of I_2 in KI in aqueous, alcoholic and acetic acid media, iodine in benzene as well as ICl in chloroform, benzene and acetic acid media respectively ; but in all cases erratic results have been obtained. Iodination has been effected successfully by gradual acidification with dilute acetic acid a mixture of compound (IV) in dilute KOH and iodine in dilute KOH. The exact position of iodine (5 to 7) has not been ascertained. Hydrochloride or hydroiodide of compound (C) ($R=C_6H_{13}$) could not be crystallised.

*EXPERIMENTAL

2 : 3-*Dimethyl*-4-*hydroxy*-8-*methoxyquinoline* (I : R=Me).—A mixture of *o*-anisidine (1 *M*), 2-methyl acetoacetic ester (1 *M*) and a few drops of HCl (dil.) was kept overnight and it was then heated in an oil-bath at 120° to 130° in a Dean and Stark apparatus till no more water had collected. Benzene was then distilled off on the oil-bath and the residual viscous mass was poured into boiling diphenyl oxide. After boiling for 15 minutes, the mass was cooled, diluted with petroleum ether (b.p. 60-80°), kept overnight, filtered and washed with fresh petroleum ether. The crude yield was 55%. It crystallised from alcohol in white needles, m.p. 289-91°. (Found : C, 70.5 ; H, 6.6. $C_{12}H_{13}O_2N$ requires C, 70.94 ; H, 6.4%).

2-*Methyl*-3-*ethyl*-4-*hydroxy*-8-*methoxyquinoline* (I : R=Et) was prepared from a mixture of *o*-anisidine and 2-ethyl acetoacetic ester in 65% yield. It was crystallised from alcohol in white needles, m.p. 288°. (Found : C, 71.5 ; H, 6.7. $C_{13}H_{15}O_2N$ requires C, 71.88 ; H, 6.91%).

2-*Methyl*-3-*propyl*^{n}-4-*hydroxy*-8-*methoxyquinoline* (I : R=Pr^n) was prepared from a mixture of *o*-anisidine and 2-propyl^n acetoacetic ester in 57% yield. It was crystallised from alcohol in white needles, m.p. 198-200°. (Found : C, 72.4 ; H, 7.1. $C_{14}H_{17}O_2N$ requires C, 72.73 ; H, 7.36%).

2-*Methyl*-3-*butyl*^{n}-4-*hydroxy*-8-*ethoxyquinoline* (I : R=Bu^n) was prepared from a mixture of *o*-anisidine and 2-butyl^n acetoacetic ester in 52% yield. It was crystallised from alcohol in white needles, m.p. 196-97°. (Found : C, 73.1 ; H, 7.5. $C_{15}H_{19}O_2N$ requires C, 73.47 ; H, 7.75%).

2-*Methyl*-3-*amyl*^{n}-4-*hydroxy*-8-*methoxyquinoline* (I : R= amyl^n) was prepared from a mixture of *o*-anisidine and 2-amyl^n acetoacetic ester in 55% yield. It was crystallised from alcohol in white needles, m.p. 165°. (Found : C, 73.9 ; H, 7.9. $C_{16}H_{21}O_2N$ requires C, 74.13 ; H, 8.12%).

2-*Methyl*-3-*hexyl*^{n}-4-*hydroxy*-8-*methoxyquinoline* (I : R=$C_6H_{13}^n$) was prepared from a mixture of *o*-anisidine and 2-hexyl^n acetoacetic ester in 42% yield. It was crystallised from alcohol in white needles, m.p. 152°. (Found : C, 74.4 ; H, 8.1. $C_{17}H_{23}O_2N$ requires C, 74.71 ; H, 8.42%).

2 : 3-*Dimethyl*-4-*chloro*-8-*methoxyquinoline* (II : R=Me).—A mixture of (I : R=Me) (15 g.), $POCl_3$ (35 c.c.) and PCl_5 (3 g.) was heated in an oil-bath at 125-30° for 5 hours. The product was then cooled and poured on ice. The aqueous solution was partly neutralised, clarified with charcoal and basified with ammonia under cooling. The chloro compound separated out in fine needles. It was crystallised

* Melting point are uncorrected.

from petroleum ether (b.p. 60-80°) in colorless fine needles, m.p. 132-33°, yield 1.4 g. (Found: C, 64.8; H, 5.3. $C_{12}H_{11}ONCl$ requires C, 65.01; H, 5.41%). The picrate crystallised from alcohol in deep yellow needles, m.p. 204-206°.

2-Methyl-3-ethyl-4-chloro-8-methoxyquinoline (II: R = Et) was crystallised from petroleum ether (60-80°) in colorless fine needles, m.p. 115°. (Found: C, 66.0; H, 5.0. $C_{13}H_{14}ONCl$ requires C, 66.24; H, 5.94%). The picrate crystallised from alcohol in yellow needles, m.p. 163-65°.

2-Methyl-3-propyl^n-4-chloro-8-methoxyquinoline (II: R = Pr^n) was crystallised from petroleum ether (b.p. 60-80°) in colorless needles, m.p. 122-23°. (Found: C, 67.0; H, 6.1. $C_{14}H_{16}ONCl$ requires C, 67.33; H, 6.41%). The picrate was crystallised from alcohol in yellow needles, m.p. 165-66°.

2-Methyl-3-butyl^n-4-chloro-8-methoxyquinoline (II: R = Bu^n) was crystallised from petroleum ether (60-80°) in colorless needles, m.p. 96-97°. (Found: C, 68.0; H, 6.6. $C_{15}H_{18}ONCl$ requires C, 68.31; H, 6.83%). The picrate was crystallised from alcohol in yellow needles, m.p. 165-67°.

2-Methyl-3-amyl^n-4-chloro-8-methoxyquinoline (II: R = amyl^n) was crystallised from petroleum ether (60-80°) in colorless needles, m.p. 101-102°. (Found: C, 68.7; H, 7.0. $C_{16}H_{20}ONCl$ requires C, 69.18; H, 7.2%) The picrate was crystallised from alcohol in yellow needles, m.p. 161-62°.

2-Methyl-3-hexyl^n-4-chloro-8-methoxyquinoline (II: R = $C_6H_{13}{}^n$) was similarly crystallised in colorless needles, m.p. 96-97°. (Found: C, 69.6; H, 7.2. $C_{17}H_{22}ONCl$ requires C, 69.98; H, 7.55%). The picrate was crystallised from alcohol in yellow needles, m.p. 130-32°.

2-β-Diethylaminoethyl-3-methyl-4-chloro-8-methoxyquinoline (III: R = Me).—A mixture of (II: R = Me) (6.6 g.), diethylamine hydrochloride (3.3 g.), paraformaldehyde (1.8 g.) and 3 drops of HCl (conc.) in absolute alcohol (10 c.c.) was heated on a water-bath. After an hour a further amount of paraformaldehyde (1 g.) was added and heating continued for another 2 hours. Alcohol was removed on a water-bath, the product was dissolved in water, basified with NaOH and the base was extracted with benzene. The benzene solution was dehydrated (Na_2SO_4) and dry HCl gas was passed in it when the hydrochloride separated out. It was then filtered and washed with dry acetone. The substance was highly hygroscopic. The *picrate* was crystallised from a large volume of alcohol in brown needles, m.p. 195-96°. (Found: N, 13.4. $C_{23}H_{26}O_8N_5Cl$ requires N, 13.07%).

The picrates of other 2-β-diethylaminoethyl-3-alkyl-4-chloro-8-methoxyquinolines (III: R = alkyl) are described in Table I. These were all crystallised from alcohol.

TABLE I

Picrate of (III). R =	Cryst. shape.	M.P.	Formula.	%Nitrogen. Found.	Calc.
Et.	Brown needles	178-79°	$C_{24}H_{28}O_8N_5Cl$	13.10	12.74
Pr^n	Yellow ,,	158-60°	$C_{25}H_{30}O_8N_5Cl$	12.60	12.43
Bu^n	,, ,,	151-52°	$C_{26}H_{32}O_8N_5Cl$	12.30	12.12
Amyl^n	,, ,,	129-30°	$C_{27}H_{34}O_8N_5Cl$	12.10	11.83
Hexyl^n	,, ,,	139-40°	$C_{28}H_{36}O_8N_5Cl$	11.40	11.55

2-β-Diethylaminoethyl-3-methyl-4-chloro-8-hydroxyquinoline (IV : R = Me).—A mixture of crude (III : R=Me) (7 g.), H_2SO_4 (conc., 50 c.c.) and water (28 c.c.) was refluxed for 6 hours. The product was then poured on ice, partly neutralised, clarified with charcoal and finally basified with NH_3 under cooling. The viscous brownish mass was then dissolved in dilute NaOH solution. On acidification with acetic acid, a semisolid hydroxy compound separated out. It developed a greenish colour with $FeCl_3$ in alcoholic solution. The *picrate* was crystallised from alcohol in yellow needles, m.p. 193-94°. (Found : N, 13.6. $C_{22}H_{24}O_8N_5Cl$ requires N, 13.43%).

Picrates of 2-β-diethylaminoethyl-3-alkyl 4-chloro-8-hydroxyquinolines (IV) were crystallised from alcohol in yellow needles. The m.p. and analysis of the picrates are recorded in Table II.

TABLE II

Picrates of (IV). R=	M.P.	Formula.	%Nitrogen. Found.	Calc.
Et	190-92°	$C_{23}H_{26}O_8N_5Cl$	13.10	13.07
Pr^n	170-71°	$C_{24}H_{28}O_8N_5Cl$	12.80	12.74
Bu^n	115-16°	$C_{25}H_{30}O_8N_5Cl$	12.30	12.43
Amyl^n	125-26°	$C_{26}H_{32}O_8N_5Cl$	12.50	12.12
Hexyl^n	126-27°	$C_{27}H_{34}O_8N_5Cl$	12.10	11.81

TABLE III

(C) R=.	Halides.	Cryst. from.	M.P.	Formula.	%Iodine. Found.	Calc.
Et	HCl	EtOH+EtAc	184-86°	$C_{17}H_{23}ON_2Cl_2I$	26.60	27.08
Et	HI	EtOH	166-68°			
Pr^n	HI	,,	177-79°	$C_{18}H_{25}ON_2Cl_2I_2$	43.80	44.20
Bu^n	HI	,,	172-73°	$C_{19}H_{27}ON_2ClI_2$	43.05	43.10
Amyl^n	HCl	EtAc+EtOH	162-64°	$C_{20}H_{29}OO_2Cl_2I$	24.20	24.85

2-β-Diethylaminoethyl-3-methyl-4-chloro-5 or *-7-iodo-8-hydroxyquinoline* (C : R= Me).—Crude (IV : R=Me) (5 g.) was dissolved in 200 c.c. of 2% KOH and filtered. To this solution was added a solution of iodine (5 g. in 100 c.c. of 3% KOH) and the mixture was gradually acidified with dilute acetic acid under stirring during a period of half an hour. The mass was left overnight, filtered, triturated with a solution of dilute $Na_2S_2O_3$ and NH_3. The pasty greenish brown mass was then dissolved in benzene, the benzene solution was dried (Na_2SO_4). *Hydrochloride* was prepared by passing dry HCl gas into the benzene solution under cooling. Monohydrochloride crystallised from a mixture of absolute alcohol and ethyl acetate, m.p. 185-86°. (Found : I, 27.1. $C_{16}H_{21}ON_2Cl_2I$ requires I, 27.9%).

The properties of hydrochlorides and hydroiodides of other 5- or 7-iodo-8-hydroxyquinolines (C) are recorded in Table III.

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CHROMATOGRAPHIC STUDY OF ANIONIC COMPLEXES. PART V. SEPARATION OF IONS IN PRESENCE OF TARTRATE USING METHANOL AS SOLVENT

By Eric John Singh and Arun Kumar Dey

Attempts to separate Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} and Fe^{3+} in mixtures by filter paper strip chromatography have been made, using tartrate as complexing agent and aqueous methanol as solvent. The effect of adding varying concentrations of the complexing agent to the solution has been studied. The R_L and R_T values have been determined in each case. In general, good separation of ions occurs when total metal to tartrate ratio is below 1 : 1; with higher concentrations of tartrate, separation is not possible. The R_L and R_T values change with the concentration of ion, and therefore their use in qualitative analysis may be regarded to be limited. But, nevertheless, we have observed that it is possible to separate the ions and detect them on filter paper qualitatively after separation. The figures show clearly the sequence of separation of the ions though the R_T values of the ion at the top merges into the R_T of the ion separating out next. These results therefore qualitatively show that the complex-forming property of the ions may be useful in the separation of these ions from mixtures.

In a number of previous publications, we have described our studies on the diffusion of various metal ions through filter paper strips in the presence of varying concentrations of different complexing agents, using aqueous alcohol as solvent (Singh and Dey, *Z. anal. Chem.*, 1958, **159**, 290, 332; 1959, **165**, 81, 179; *J. Chromatog.*, 1959, **2**, 95; 1960, **3**, 146; *Proc. Nat. Acad. Sci., India*, 1959, **28A**, 43, 87).

In the present communication we have extended the studies to separations using aqueous methanol as solvent and recorded only some of the typical observations out of a very large number of experiments.

Experimental

Standard solutions of sodium tartrate, cupric sulphate, cobalt sulphate, nickel sulphate, ferric sulphate and cadmium chloride were prepared, using reagent grade chemicals. The method adopted was the strip filter paper chromatographic technique, using an arrangement described by Gage, Douglass and Wender (*J. Chem. Ed.*, 1950, **27**, 159). Various concentrations of methanol were tried and 50% methanol was found suitable as a solvent for the separations. A series of mixtures containing equal concentrations of metal solutions with varying proportions of sodium tartrate were prepared, keeping the total volume constant. The ratio of the total concentration of the metals (obtained by adding the concentrations in molarity of the metals) to the concentration of tartrate added is expressed as the metal : tartrate ratio (equivalents of tartrate). The mixtures were spotted on filter paper strips, prepared from Whatman filter paper No. 1. The chromatograms were run at a constant temperature in a room, with temperature controlled at 30°, and the time allowed was 1.5 hours for diffusion.

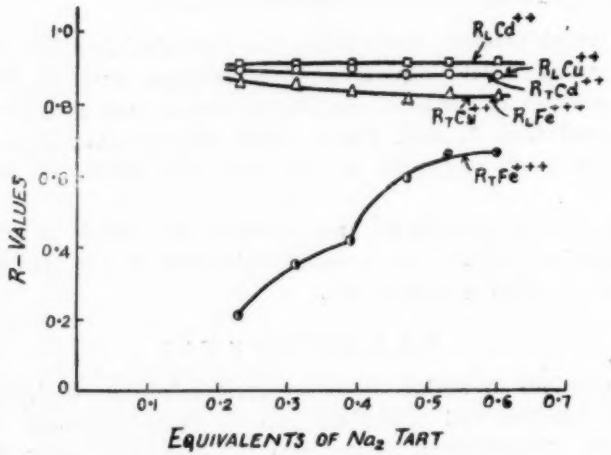
In order to ascertain whether a good separation is taking place in mixtures or whether overlapping is occurring between two ions, R_L and R_T values instead of R_f values are often useful (Majumdar and Chakrabarty, *Anal. Chim. Acta*, 1957, **17**, 415). So we have determined these values and considered them.

For the economy of space, the experimental tables have been omitted and figures showing the variation of the R-values with the concentration of tartrate employed in some typical cases have only been reported.

Separation of Cu^{2+}, Cd^{2+} *and* Fe^{3+}

The final concentration of each of the metal ions was 0.042 *M* and a mixture of H_2S-water and $K_4Fe(CN)_6$ solution was used for developing. The results are plotted in Fig. 1. The separation of Cd^{2+}, Cu^{2+} and Fe^{3+} ions is possible when 0.234 to 0.60 equivalents of tartrate are used. When the ratio of metal : concentration of tartrate is 1 : 0.7 to 1 : 0.9, the Fe^{3+} ions are found to diffuse into those of copper (II). With a ratio 1 : 1 to 1 : 1.6, there is only a separation of the Cd^{2+} ions, and with higher concentrations

FIG. 1



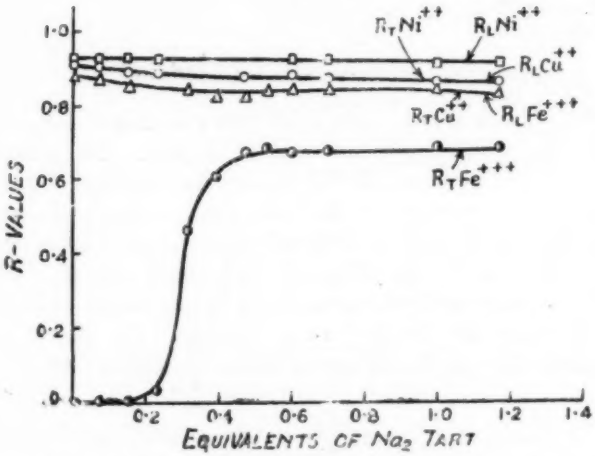
of the same, separation is not possible. It was noted that the R_L values of Cd^{2+} do not change appreciably with the additions of tartrate. The R_L values of Cu^{2+} do not change with small additions of tartrate, but gradually decrease with higher concentrations of the same. The R_L values of Fe^{3+} initially decreased with the addition of tartrate, but afterwards they tended to become constant. The R_T value of Fe^{3+} became constant with higher concentrations of the complexing agent.

Separation of Ni^{2+}, Cu^{2+} *and* Fe^{3+}

The final concentration of each of the metal ions was 0.042 *M* and a mixture of dimethylglyoxime and $K_4Fe(CN)_6$ solutions was used for developing. The separation

of Ni^{2+}, Cu^{2+} and Fe^{2+} ions (Fig. 2) is possible up to the addition of 1.17 equivalents of tartrate. With higher concentrations of the same, separation is not possible. A good separation was obtained when 0.313 to 0.6 equivalents of tartrate were used. It was noted that the R_L values of Ni^{2+} did not change with small additions of tartrate but

FIG. 2

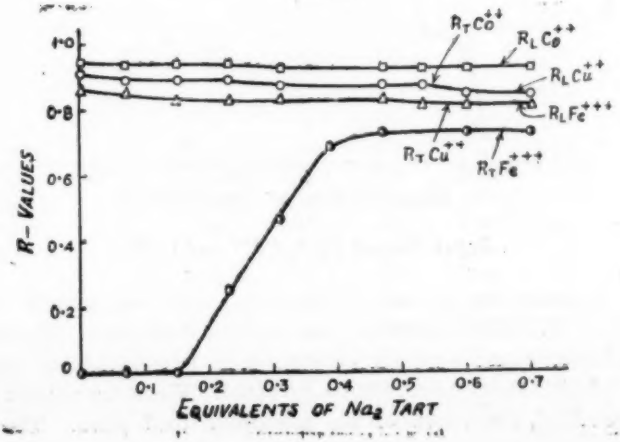


decreased slightly with higher concentrations of the complexing agent. The R_L values of Cu^{2+} decreased slightly with the additions of the complexing agent. The R_L and R_T values of Fe^{2+} behave in a similar manner as in Fig. 1.

Separation of Cu^{2+}, Co^{2+} *and* Fe^{2+}

The final concentration of each of the metal ions was 0.042*M* and a mixture of H_2S-water and $K_4Fe(CN)_6$ solution was used for developing. The separation of Co^{2+} Cu^{2+} and Fe^{2+} (Fig. 3) is possible up to the addition of 0.70 equivalents of complexing

FIG. 3

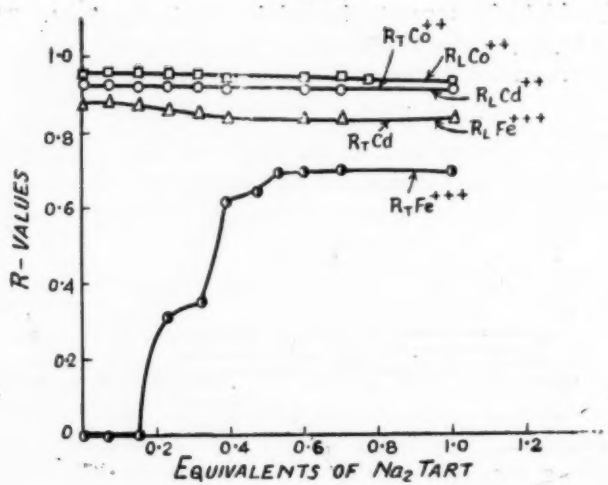


agent. With increase in the concentrations of the same, no separation is possible. A good separation was obtained when 0.156 to 0.6 equivalents of the complexing agent were added. It was noted that the R_L values of Co^{2+} and Fe^{3+} decreased slightly with the additions of the complexing agent and finally tended to become constant with higher concentrations of tartrate ions. The R_T value of Fe^{3+} became constant with 0.47 equivalents of the complexing agent.

Separation of Fe^{3+}, Co^{2+} *and* Cd^{2+}

The final concentration of each of the metal ions was 0.042*M* and a mixture of H_2S-water and $K_4Fe(CN)_6$ solution was used for developing. The separation of Co^{2+}, Cd^{2+} and Fe^{3+} ions (Fig. 4) was effected up to the addition of one equivalent of tartrate. With higher concentrations of the same, no separation was possible. A good separation was obtained when 0.078 to 0.766 equivalents of the complexing agent were added. It was seen that the R_L values of Co^{2+}, Cd^{2+} and Fe^{3+} did not change with small addition of the complexing agent, but by increasing the concentration of the same, the values decreased and finally became constant. The R_T values of Co^{2+} and Cd^{2+} became constant with 0.39 equivalents of the complexing agent.

FIG. 4

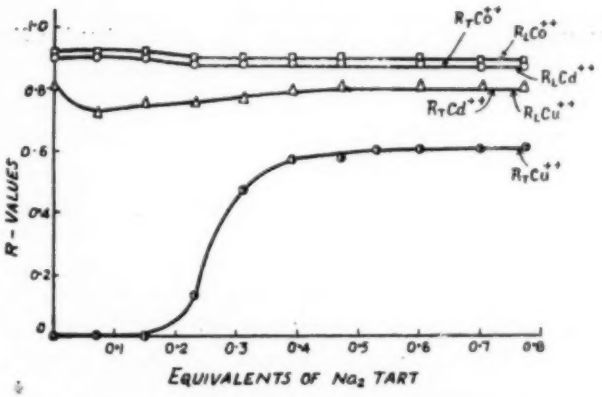


Separation of Cu^{2+}, Cd^{2+} *and* Co^{2+}

The final concentration of each of the metal ions was 0.042*M* and a mixture of H_2S-water and $K_4Fe(CN)_6$ solution was used for developing. No precipitate was obtained in the beginning up to 0.234 equivalents of tartrate added, but with higher concentrations of the same, precipitation occurred. When 1.2 or more equivalents of the tartrate were added, dissolution of the precipitate took place. The separation of

Co^{2+}, Cd^{2+} and Cu^{2+} ions (Fig. 5) was effected up to 0.77 equivalents of tartrate added. A good separation was obtained when 0.234 to 0.53 equivalents of the complexing agent were added. It was seen that the R_L values of Co^{2+} and Cd^{2+} did not change with small additions of the complexing agent. These values gradually decreased with the increase

FIG. 5



in the concentration of the complexing agent and had a tendency to become constant when large proportions of the same were employed. The R_T values of Cd^{2+} and Cu^{2+} became constant with 0.47 and 0.53 equivalents of the complexing agent respectively.

Separation of Fe^{3+}, Cu^{2+}, Cd^{2+} *and* Co^{2+}

The final concentration of each of the metal ions was 0.031*M* and a mixture of H_2S-water and $K_4Fe(CN)_6$ solution was used for developing. A typical table of separation is shown below.

TABLE I

No.	Ratio of total metal : $Tart^{3-}$.	Cobalt (II). R_L.	Cobalt (II). R_T.	Cadmium (II). R_L.	Cadmium (II). R_T.	Copper (II). R_L.	Copper (II). R_T.	Iron (III) R_L.	Iron (III) R_T.
1	1 :0.00	0.95	0.93	0.93	0.91	0.91	0.84	0.84	0.00
2	1 :0.05	0.95	0.93	0.93	0.90	0.90	0.80	0.80	0.00
3	1 :0.10	0 94	0.92	0.92	0.89	0.89	0.79	0.79	0.00
4	1 :0.15	0.94	0.92	0.92	0.89	0.89	0.80	0.80	0.00
5	1 :0.25	0.94	0.92	0.92	0.89	0.88	0.80	0.80	0.25
6	1 :0.30	0.94	0.92	0.92	0.88	0.88	0.80	0.80	0.33
7	1 :0.35	0.94	0.92	0.92	0.88	0.88	0.81	0.80	0.37
8	1 :0.40	0.94	0.92	0.92	0.88	0.88	0.81	0.80	0.40
9	1 :0.45	0.94	0.91	0.92	0.88	0.87	0.80	0.80	0.42
10	1 :0.50	0.94	0.91	0.91	0.87	0.87	0.80	0.80	0.47
11	1 :0.55	0.94	0.91	0.91	0.85	0.85	0.79	0.79	0.51
12	1 :0.60	0.94	0.91	0.91	0.85	0.85	0.79	0.79	0.54
13	1 :0.65	0 94	0.91	0.91	0.84	0.84	0.78	0.78	0.57

The separation of Co^{2+}, Cd^{2+}, Cu^{2+} and Fe^{3+} ions is possible up to 0.8 equivalents of tartrate added. With higher concentrations, no separation occurs.

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SYNTHESIS OF NEW LOCAL ANAESTHETICS. PART II

By Prithwi Nath Bhargava and Parashu Ram Singh

Piperidinoacetyl-2-amino-4-phenyl-, -4-*p*-chlorophenyl-, -4-*p*-aminophenyl-, -4-methyl-, -4-chloromethyl-, -4 : 5-dimethyl- and -4-methyl-5-ethyl thiazoles have been synthesised and their local anaesthetic activity tested. The hydrochlorides of piperidinoacetyl-2-amino-4-methyl-5-ethyl- -4-*p* chlorophenyl- and -4-*p*-aminophenyl-thiazoles have been found to be active local anaesthetics.

In continuation of the previous work (Bhargava and Nair, this *Journal*, 1957, **34**, 42), 2-amino-4-phenyl-, -4-*p*-chlorophenyl-, -4-*p*-aminophenyl- -4-methyl-, -4-chloromethyl-, -4 : 5-dimethyl- and -4-methyl-5-ethyl-thiazoles were prepared as the starting materials, which were in the first stage condensed with chloroacetyl chloride to obtain the corresponding chloroacetylamino compounds. These were further condensed with a secondary amine, piperidine. The hydrochlorides of these bases have been prepared and their local anaesthetic activity has been tested by frog's sciatic plexus method.

A study of the pharmacological screening (Bulbring and Wajda, *J. Pharmacol.*, 1945, **85**, 78) shows that the hydrochlorides of piperidinoacetyl-2-amino-4-methyl-5-ethyl-, -4-*p*-chlorophenyl- and -4-*p*-aminophenyl-thiazoles are the most active of these compounds. The values obtained for these are less than that for procaine hydrochloride. It is found that an extra amino group and a chlorine atom in *para* position in the benzene nucleus confer more activity on the compound than the presence of a higher aromatic nucleus. The simple benzene nucleus enhances the solubility and volatility of the compound as compared with other condensed rings.

Experimental

2-Amino-4 or 4 : 5-substituted thiazoles were prepared according to the method of Dodson and King (*J. Amer. Chem. Soc.*, 1945, **67**, 2242). Properties and analytical data of these are recorded in Table I.

Table I

2-Aminothiazoles.

[T denotes thiazole. A denotes 2-amino-].

	Compounds.	% Yield.	Colour.	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	A-4-phenyl-T*	68	Yellow	147°	$C_9H_8N_2S$	19.35	19.94
2.	A-4-*p*-chlorophenyl-T†	70	,,	164°	$C_9H_7N_2ClS$	15.03	15.13
3.	A-4-*p*-aminophenyl-T†	72	,,	174°	$C_9H_9N_3S$	16.70	16.75
4.	A-4-methyl-T*	56	Brown	126°	$C_4H_6N_2S$	27.85	28.06
5.	A-4-chloromethyl-T	52	,,	123°	$C_4H_5N_2ClS$	17.10	17.17
6.	A-4 :5-dimethyl-T	48	,,	131°	$C_5H_8N_2S$	24.85	25.00
7.	A-4-methyl-5-ethyl-T	36	,,	135°	$C_6H_{10}N_2S$	22.30	22.53

* Dodson and King, *loc. cit.*
† King and Hlaveck, *J. Amer. Chem. Soc.*, 1950, **72**, 3722.

Chloroacetyl-2-amino-4-phenylthiazole.—Chloroacetyl chloride (3 c.c.), dissolved in dry benzene (12 c.c.), was gradually added to 2-amino-4-phenylthiazole (5 g.), dissolved in benzene (30 c.c.). The reaction mixture was warmed at 70° on a water-bath for 1½ hours. Benzene was distilled off and the residue washed with sodium bicarbonate solution, then with water, and dried. The product was crystallised from alcohol in light yellow crystals, m.p. 157°.

Other chloroacetyl-2-aminothiazoles were similarly prepared. Properties and analytical data of these are recorded in Table II.

TABLE II

Chloroacetyl-2-aminothiazoles.

	Compound.	% Yield.	Colour.	M.P.	Formula.	% Chlorine. Found.	Calc.
1.	-A-4-phenyl-T	72	Light yellow	157°	$C_{11}H_9ON_2ClS$	13.92	14.06
2.	-A-4-*p*-chlorophenyl-T	78	Do	118°	$C_{11}H_8ON_2Cl_2S$	24.00	24.39
3.	-A-4-*p*-aminophenyl-T	82	Yellowish green	187°	$C_{11}H_{10}ON_3ClS$	13.42	13.27
4.	-A-4-methyl-T	68	Brown	211°	$C_6H_7ON_2ClS$	18.54	19.06
5.	-A-4-chloromethyl-T	64	Brownish black	121°	$C_6H_6ON_2Cl_2S$	31.08	31.11
6.	-A-4:5-dimethyl-T	71	Brown	119°	$C_7H_9ON_2ClS$	17.25	17.38
7.	-A-4-methyl-5-ethyl-T	65	Do	120°	$C_8H_{11}ON_2ClS$	16.32	16.40

Piperidinoacetyl-2-amino-4-phenylthiazole.—To chloroacetyl-2-amino-4-phenylthiazole (5 g.) in absolute alcohol (50 c.c.) piperidine (3.5 c.c.) was added and the mixture refluxed for 4 to 5 hours. Alcohol and excess of piperidine were recovered by distillation and the residue was washed with sodium bicarboante solution and finally with water. The product was crystallised from 50% alcohol and recrystallised from benzene in brown crystals, m.p. 167°. Similarly piperidinoacetyl derivatives of other 2 amino thiazoles were prepared. Their properties and analytical data are shown in Table III

TABLE III

Piperidinoacetyl-2-aminothiazoles and their hydrochlorides.

	* Piperidino derivatives of compounds.					Hydrochlorides		
				% Sulphur.			% Chlorine.	
No.	Colour.	M.P.	Formula.	Found.	Calc.	M.P.	Found.	Calc.
1.	Brown	167°	$C_{16}H_{19}N_3S$	10.75	10.97	254°	10.92	11.04
2.	Do	109°	$C_{16}H_{18}N_3ClS$	9.85	10.00	130°	19.06	19.56
3.	Do	152°	$C_{16}H_{20}N_4S$	10.50	10.67	245°	10.43	10.69
4.	Brownish black	114°	$C_{11}H_{17}N_3S$	14.26	14.35	119°	13.50	13.71
5.	Do	107°	$C_{11}H_{16}N_3ClS$	12.30	12.44	165°	23.25	23.86
6.	Black	132°	$C_{12}H_{19}N_3S$	13.45	13.50	153°	12.65	12.98
7.	Do	109°	$C_{13}H_{21}N_3S$	12.50	12.75	123°	13.50	13.71

* The related compounds as recorded in Table II.

Pharmacological screening.—The hydrochlorides of 2-amino-4 or 4:5-substituted thiazoles were screened for local anaesthetic activity by frog's sciatic test. Two frogs were tested for each compound in 0.1 and 0.2% concentration and the time taken by a given concentration of local anaesthetic to fail to provoke withdrawal of foot was recorded. The results are shown in Table IV.

TABLE IV

Results of local anaesthesia.

Hydrochlorides.	Onset of anaesthesia in		Onset of anaesthesia	
	0.1*N*-HCl.	0.2*N*-HCl.	0.1*N*-HCl.	0.2*N*-HCl.
	A. Conc. of anaesthesia =0.1%.		B. Conc. of anaesthesia =0.2%.	
1. Procaine	15 mins.	20 mins.	12 mins.	14 mins.
2. Pa-A-4-phenyl-T	16	20	13	16
3. Pa-A-4-*p*-chlorophenyl-T	10	14	9	12
4. Pa-A-4-*p*-aminophenyl-T	12	15	10	13
5. Pa-A-4-methyl-T	17	22	15	18
6. Pa-A-4-chloromethyl-T	14	17	13	15
7. Pa-A-4:5-dimethyl-T	13	16	12	13
8. Pa-A-4-methyl-5-ethyl-T	10	14	8	10

N.B. Pa stands for piperidinoacetyl.

Thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

CHEMISTRY DEPARTMENT,
COLLEGE OF SCIENCE B H U
VARANASI.

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SHORT NOTES

NEW ROUTE FOR THE PREPARATION OF 3-HYDROXY*cyclo*HEXANEMETHANOL

By M. A. Karim

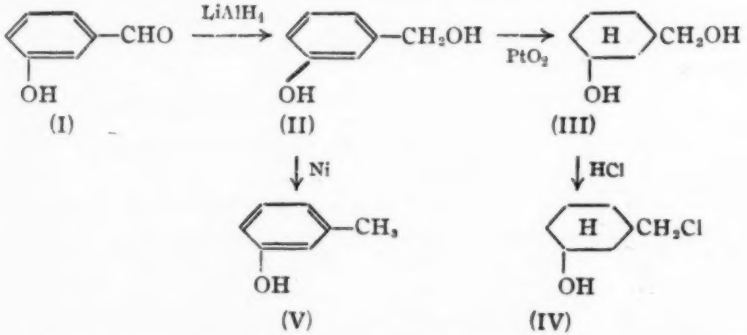
Von den Velden (*J. prakt. Chem.*; 1877, **15**, 165) first prepared *m*-hydroxybenzyl alcohol by the reduction of *m*-hydroxybenzoic acid with sodium amalgam. Mettler (*Ber.*, 1905, **38**, 1752) obtained the same alcohol in 45% yield by following the above method.

Lapworth and Showsmith (*J. Chem. Soc.*, 1922, **121**, 1395) improved the yield to 80% by the reduction of *m*-hydroxybenzaldehyde with sodium amalgam. The present author has obtained the product in 82% yield by an alternative method, involving the reduction of *m*-hydroxybenzaldehyde with lithium aluminium hydride.

The preparation of 3-hydroxy*cyclo*hexanemethanol (stereoisomers), and that of *cis*- and *trans*- diol, separately, have been reported by different authors from 3-hydroxy*cyclo*hexane carboxylic acid and its derivatives (Clark and Owen, *ibid.*, 1950, 2103; Goering and Serres, *J. Amer. Chem. Soc.*, 1952, **74**, 5908; Noyce and Denny, *ibid.*, p. 5912; 1954, **76**, 769; Parkin and Tattershall, *J. Chem. Soc.*, 1907, **91**, 480).

The present work describes the devised method for the preparation of 3-hydroxybenzyl alcohol and its hydrogenation at room temperature and pressure over platinum oxide catalyst to 3-hydroxy*cyclo*hexanemethanol.

The attempted method for the hydrogenation of 3-hydroxybenzyl alcohol over Raney nickel catalyst was not successful as the resultant product was mostly *m*-cresol.



m-Hydroxybenzyl Alcohol (II).—*m*-Hydroxybenzaldehyde (25 g.), dissolved in ether (300 c.c.), was added dropwise to a gently refluxing solution of $LiAlH_4$ (5 g.) in ether (500 c.c.) in a three-necked flask, fitted with a mercury-sealed stirrer and condenser ($CaCl_2$-guard tube). The reaction mixture was allowed to reflux for 3 hours,

cooled in ice and the excess $LiAlH_4$ was destroyed by dropwise addition of ice-cold water. The precipitated inorganic hydroxides were dissolved by the dropwise addition of ice-cold 10% H_2SO_4. The mixture was extracted with ether and the ether extract washed with sodium bisulphite solution to remove the unchanged aldehyde, followed by sodium bicarbonate and finally water to remove the acid completely.

The ether extract was dried over anhydrous sodium sulphate and the solvent removed. The residue was recrystallised from benzene, yield 20.5 g. (82%), m.p. 68.5-69° (lit. 67.73°). (Found: C, 77.52; H, 7.52. Calc. for C_7H_8O: C, 77.77; H, 7.40%).

Attempted Hydrogenation of (II).—*m*-Hydroxybenzyl alcohol (50 g.) was dissolved in a solution of NaOH (15 g. in 50 c.c. water) and the volume made up to 95 c.c. with water. Raney nickel catalyst (6 g.) was then added and the mixture hydrogenated at 150° and 238 mm for 2 hours. The cooled, filtered and acidified solution was extracted with ether and after drying over anhydrous sodium sulphate, the ether was removed. The product was crude *m*-cresol (V), confirmed by the preparation and combustion analysis of the nitro (m.p. 102-103-5°) and bromo (m.p. 82-83°) derivatives.

3-*Hydroxy*cyclo*hexanemethanol*.—To the alcohol (II, 5 g.), dissolved in ethanol (50 c.c.), platinum oxide catalyst (0.15 g.) was added and the mixture hydrogenated for 40 hours, during which period the theoretically required volume of hydrogen was absorbed. The catalyst was removed by filtration and the solvent by distillation under reduced pressure. The residue was distilled *in vacuo*, yield 4.5 g. (81%); b.p. 115-20°/0.5 mm; n_D^{20} 1.4900 (lit. 1.4900). (Found: C, 64.40; H, 10.95. Calc. for $C_7H_{14}O_2$: C, 64.60; H, 10.85%).

3-*Hydroxy*cyclo*hexanemethyl chloride* (IV) was prepared from (III) in 78% yield according to the method of Clark and Owen (*loc. cit.*), b.p. 125-35°/30 mm; n_D^{24} 1.4910 (lit. 1.4910). (Found: C, 56.26; H, 9.01; Cl, 23.5. Calc. for $C_7H_{13}OCl$: C, 56.56; H 8.9; Cl, 23.8%).

CENTRAL TESTING LABORATORIES,
KARACHI, W. PAKISTAN.

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4:6-DINITRO-*o*-TOLUIDINE: A NEW SYNTHESIS

By R. S. Kapil*

During a programme of research on nitration of some iodo compounds in this laboratory (Kapil, *J. Chem. Soc.*, 1959, 4127), sufficient quantity of 4:6-dinitro-*o*-toluidine was required. Considerable difficulty was experienced when its preparation was undertaken by the partial reduction of 2:4:6-trinitrotoluene (Anschütz and Zimmermann, *Ber.*, 1915, **48**, 152; Brand and Eisenmenger, *Ber.*, 1916, **49**, 674); other side-products, such as, 6-nitro-*m*-toluylenediamine (Tiemann, *Ber.*, 1870, **3**, 217; Brady *et al.*, *J. Chem. Soc.*, 1929, 2264), 2:6-dinitro *p*-toluidine (Holleman and Boeseken, *Rec. trav. chim.*, 1897, **16**, 425; Brady *et al.*, *loc. cit.*) and 2:6-dinitro-4-hydroxylaminotoluene (Cohen and Dakin, *J. Chem. Soc.*, 1905, **87**, 1257; Anschütz and Zimmermann, *loc. cit.*), were invariably formed during reduction which were difficult to separate. A new method was therefore planned involving the nitration of 4-nitro-*o*-toluidine in concentrated sulphuric acid with fuming nitric acid.

Procedure.—To a solution of 4-nitro-*o*-toluidine (5 g.) in H_2SO_4 (*d* 1.8, 40 c.c.), cooled to 0°, fuming nitric acid (*d* 1.5, 5 c.c.) was added dropwise with vigorous shaking; the mixture was then allowed to attain the room temperature (2 hours) and poured on crushed ice. The crude 4:6-dinitro-*o*-toluidine, originally precipitated as a gummy mass, soon solidified, which was filtered, washed well with water and recrystallised from glacial acetic acid in yellow crystals (3 g.), m.p. 160°. (Found: N, 21.1. Calc. for $C_7H_7O_4N_3$: N, 21.3%).

The author wishes to express his gratitude to Dr. Shyam Sunder Joshi, D.Sc., for his kind interest in this work.

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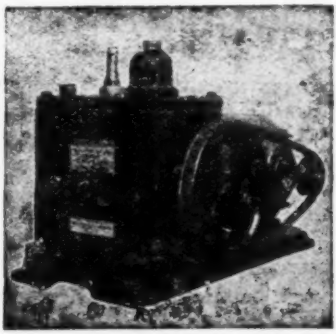

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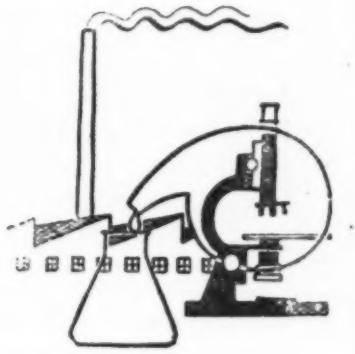

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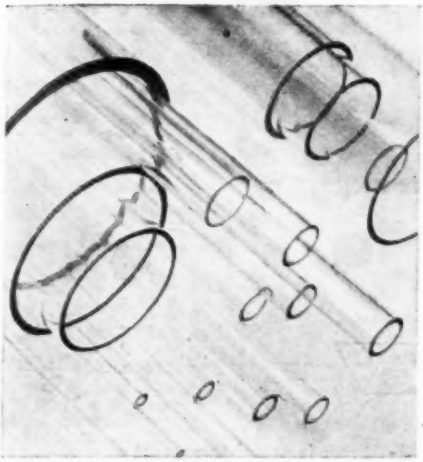

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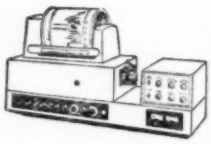

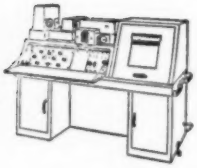

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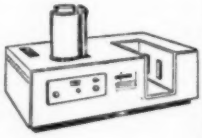

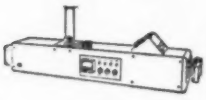

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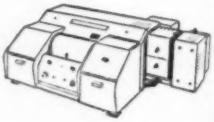

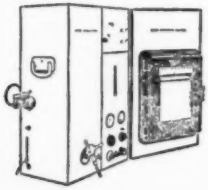

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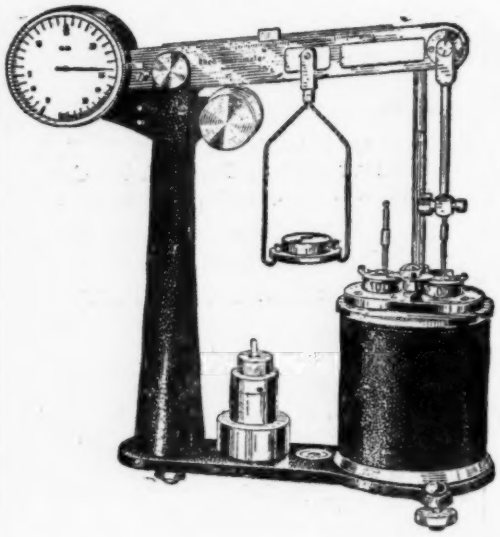

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